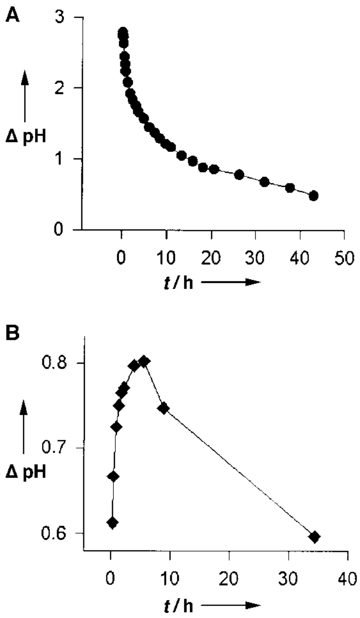

Figure 3. Evolution of the proton gradient between the two compartments after a pH jump in solutions (A) containing only liposomes and (B) containing liposomes and Chol-ATP.

proton gradient in the presence of Chol-ATP was observed, reflecting the hydrolysis of Chol-ATP and thus the release of the intravesicular ATP (Figure 3B).

In summary, we have demonstrated that ATP bearing a cholesteryl moiety at the γ-phosphate group can be transported across the membrane bilayer. It is now of interest to evaluate these model drug carriers of adenosine and various therapeutic nucleosides in integrated systems or living cells.

Experimental Section

Cholesteryloxycarbonyl-adenosine 5′-triphosphate: White powder. The ^{1}H NMR spectrum (D_2O) showed the characteristic signals of adenosine; protons of the cholesteryl moiety were observed between $\delta = 2.05$ and 0.57. ^{31}P NMR (D_2O, proton-decoupled, pH 7.1): $\delta = -10.35$ (d, α-P, $J_{P,P} = 19.8$ Hz), -18.82 (br, γ-P), -21.51 (br, β-P). Mass spectrum (electrospray): calcd for $C_{38}H_{60}N_5O_{15}P_3(NBu_3)_3$: 919.33; found 919.4. HPLC (gradient: 5–70 % acetonitrile in 0.01 M triethylammonium acetate, pH 7): t_{ret} 17.04 min. Chol-ATP ($HNBu_3$ or Na salt) is freely soluble in water and organic solvents (dichloromethane, acetonitrile, alcohols).

Vesicles preparation: SUV of defined size were prepared by reverse-phase evaporation using a mixture of egg phosphatidylcholine and phosphatidic acid (mole ratio 9:1) according to Rigaud and Pitard.[10] The phosphate-buffered solution referred to in the text contained KH_2PO_4 (20 mM), K_2SO_4 (15 mM), and Na_2SO_4 (15 mM) at pH 5.0 (90 % H_2O/10 % D_2O). After extrusion through 200-nm nucleopore membranes, the final lipid concentration was about 30 mg mL^{-1}. For the preparation of liposomes with entrapped ATP, the same procedure was applied in the presence of ATP 50 mM, and external ATP was finally thoroughly removed by filtration of the SUV through pD 10 columns (Pharmacia).

^{31}P NMR experiments: ^{31}P NMR spectra were recorded on a Bruker DMX-300 operating at 121.49 MHz, and referenced relative to external H_3PO_4 85 %. Two levels of broad band proton decoupling were applied for all the experiments. Samples were prepared immediately prior to use. In a glass vial, Chol-ATP (9 mg) was directly dissolved in the SUV preparation (550 μL, lipid concentration 30 mg mL^{-1}, phosphate-buffered solution pH 5.0, 90 % H_2O/10 % D_2O). After quick introduction into the spectrometer, an initial ^{31}P NMR spectrum ($t = 0$) was recorded (90° pulse 6 μs, relaxation delay 5 s, 16 scans). In general, successive short spectra (16 to 64 scans) were acquired at the beginning of the incubation to monitor the pH gradient development. Better signal-to-noise spectra (512 scans) were then recorded to monitor the slow kinetics of internalization and hydrolysis of Chol-ATP. The pH jump was performed by injection of a few microliters of NaOH 1 N into the NMR tube.

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Ca_2AuN: A Nitride Containing Infinite Zigzag Gold Chains**

Paul F. Henry and Mark T. Weller*

Previous investigation of the calcium–gold–nitrogen ternary phase field[1] resulted in the characterization of Ca_3AuN,[2] which crystallizes with the cubic perovskite structure. This structural type is well represented in nitride chemistry, for example Ca_3XN (X = P, As, Sb, Bi, Ge, Sn, and Pb).[3] The nitrogen atom in these compounds is surrounded

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by an octahedron of calcium atoms; the octahedra share corners and are linked into a three-dimensional framework. Here we report the synthesis of a new ternary calcium auride nitride with the formula $(Ca^{2+})_2Au^{-}N^{3-}$ by using high-pressure techniques, and its structural characterization from Rietveld refinement of powder neutron and X-ray diffraction data. Full details of the structural determination will be presented elsewhere.[4]

Atomic data and thermal displacement parameters are given in Tables 1 and 2, respectively. The most distinctive feature of the refined structure is the presence of infinite, planar zigzag gold chains parallel to the crystallographic *c* axis (Figure 1). However, the anisotropic thermal component U_{11} of the gold atom is relatively large (0.0396(7) Å^2), possibly reflecting minor buckling of the chains, but attempts to disorder the gold sites gave unstable refinements. The chains are regular with inter-gold bond lengths of 2.857(1) Å, slightly shorter than those found in metallic gold (2.884 Å). The Au-Au-Au bond angle is 118.80(7)°. The coordination sphere of gold is completed by seven contacts to calcium in the range 3.137(2)–3.242(7) Å (Figure 2). Within each gold layer the successive gold chains are stacked in phase separated by the atomic distance *a*; the gold chains within successive layers are related by a translation of ½*a*+½*b*. The Ca–N contacts of 2.431(1)–2.490(1) Å are very close to those found in α-Ca_3N_2 (2.451(2)–2.482(2) Å).[5]

Table 1. Refined atomic data for Ca_2AuN. Space group *Cmcm*; $a = 3.58139(4)$, $b = 18.06421(19)$, $c = 4.91905(5)$ Å.

Atom	Wyckoff site	*x*	*y*	*z*	$(U_i/U_{eq}) \times 100$ [Å^2]
Au	4*c*	0	0.04026(6)	¼	2.06
Ca1	4*c*	0	0.39767(9)	¼	1.36
Ca2	4*c*	0	0.21499(8)	¼	0.95
N	4*c*	0	– 0.19337(4)	¼	0.84

Table 2. Anisotropic displacement parameters [Å^2 × 100].[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au	3.96(7)	1.26(5)	0.96(5)	0	0	0
Ca1	1.39(7)	1.10(7)	1.59(8)	0	0	0
Ca2	0.90(7)	0.99(8)	0.96(7)	0	0	0
N	0.86(4)	0.66(4)	1.00(4)	0	0	0

[a] The anisotropic displacement factor exponent takes the form: $[h^2a^{*2}U_{11} + \ldots + 2hka^{*}b^{*}U_{12} + \ldots]$.

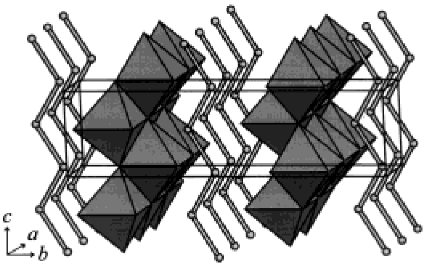

Figure 1. View of the refined structure of Ca_2AuN illustrating the zigzag gold chains parallel to the *c* axis, and the edge-sharing Ca_6N octahedra.

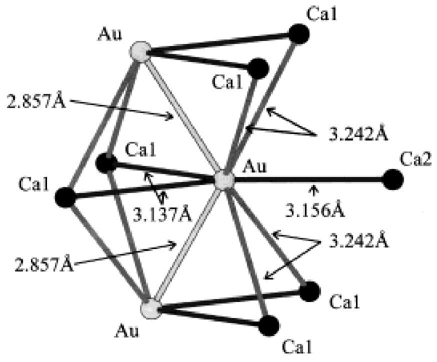

Figure 2. Environment of a gold atom in Ca_2AuN showing the ninefold coordination: two contacts to gold and seven contacts to calcium.

In solid-state materials containing gold–gold bonding, the known structural motifs are: linear chains (e.g., $KAuO_2$[6]), two-dimensional planes (e.g., Au_2Th[7]), dimeric species (e.g., EuAuGe[8]), and complex three-dimensional frameworks (e.g., corner-sharing double tetrahedra in $K_4Au_7Ge_2$).[9] Zigzag chains have been reported in the binary alloy CaAu,[10] although it has not been fully structurally characterized. Some materials containing Au^{-} ions have been shown to behave as pseudo-halides (e.g., Cs_3AuO[11] and CsAu[12]) and, therefore, it was thought that Ca_2AuN would be isotypic with Ca_2NCl.[13] However, the refined structure of Ca_2AuN is more closely related to that of CaAu as the gold environment in each material is almost identical. Ca_2AuN is best described as CaN zigzag chains inserted into the CaAu structure. Thus, Ca_2AuN is the first example of a ternary material containing zigzag gold chains and is only the second example of a gold nitride.

It was also found that the known cubic perovskite material, Ca_3AuN, could not be synthesized by the high-pressure route. Attempts led to the formation of Ca_2AuN, Ca_3N_2, and a small amount of a cubic phase related to Ca_3AuN by a doubling of *a*.

Experimental Section

A polycrystalline sample of Ca_2AuN was prepared by reaction of Ca_3N_2 powder (Aldrich, 99+%) and gold foil (99.99+%) in the correct stoichiometric ratio under high-pressure dry nitrogen (BOC, 99.999%). Due to the air and moisture sensitivity of nitrides all materials were handled in a dry nitrogen atmosphere glovebox. Ca_3N_2 and small pieces of gold foil were mixed intimately, loaded into an alumina crucible, which was then placed in a Nimonic pressure vessel,[14] and sealed. The bomb was attached to a high-pressure nitrogen supply, flushed, and then filled with the required pressure of dry nitrogen, ranging from 100 bar to 200 bar. The sample end of the bomb was heated in a tube furnace at 820°C for 3 days then cooled to room temperature and the sample reground; at the reaction temperature the pressure in the system was approximately double the initial pressure. A second heat treatment was applied, under the same conditions as before, for a further 16 h followed by cooling to room temperature at a rate of 3°C min^{-1}. No reaction of the product with the alumina crucible was apparent and the resultant powder was dark gray in color. The series of experiments at various initial pressures of 100–200 bar produced identical products.

Powder X-ray diffraction data were collected by using a Siemens D5000 diffractometer ($Cu_{K\alpha 1}$ radiation). Lattice parameters were obtained by indexing with the PC software program TREOR90.[15] Powder neutron diffraction data were collected on the POLARIS diffractometer at the ISIS spallation neutron source, Rutherford Appleton Laboratory, at room temperature. Rietveld refinement was carried out on the data collected in the high-resolution 145° detector bank, by using the GSAS suite of programs.[16] Nitrogen content, measured from C,H,N analysis, showed the nitrogen stoichiometry to be 1.01(3), assuming a Ca:Au ratio of 2:1.

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Proof of Potassium Ions by Luminescence Signaling Based on Weak Gold–Gold Interactions in Dinuclear Gold(I) Complexes**

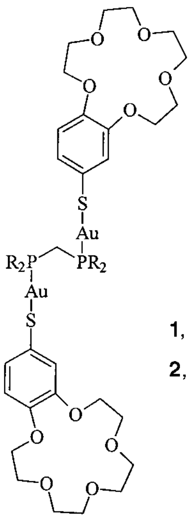
Vivian Wing-Wah Yam,* Chi-Kwan Li, and Chui-Ling Chan

The search for host molecules that can selectively recognize specific guest molecules at their receptor site and produce a measurable physical change is currently of immense interest. Spectroscopic detection of metal ions or anions is of great importance both in classical analytical chemistry and in the molecular design of ion sensors that involve optical signal transformation. The utilization of sensitive luminescence signaling has always been an attractive and popular option, particularly when combined with a selective and specific complexing process involving the target species. Ion-controlled luminescence probes are of interest for ion sensing as well as for the construction of molecular optoelectronic switches.[1–3] A number of ion-binding organic receptors have been studied, most of which were based on polyaromatic luminophores[2a, c, 4] and the exploitation of photoinduced electron transfer (PET) processes.[1–3] Although there has been increased attention given to the design of metalloreceptors in recent years, most of it has focused on systems with metal-to-ligand charge-transfer (MLCT) excited states,[5] with relatively few studies of other systems.[5a, b, 6]

In recent years there has been a growing interest in the study of polynuclear gold(I) complexes, in particular with regard to the phenomenon of aurophilicity associated with these complexes, which results from weak gold–gold interactions.[7] Recent studies by us[8] and others[9] have shown that the presence of weak gold–gold interactions in a number of di- and polynuclear gold(I) complexes gives rise to unique electronic spectroscopic features; in particular many of them exhibit intense yellowish green to orange-red phosphorescence. In general, we and others observed that an increase in gold–gold interactions leads to a lower energy emission.

Herein, we describe a versatile luminescence ion probe for potassium ions based on the switching on and off of the gold–gold interactions. The present system not only serves as a molecular phosphorescent ion sensor and a molecular optoelectronic switch, but also provides spectroscopic evidence for potassium ion induced gold–gold interactions.

The complexes [Au_2(dppm)(S-benzo[15]crown-5)$_2$] (**1**) and [Au_2(dcpm)(S-benzo[15]crown-5)$_2$] (**2**) were synthesized by the reaction of [Au_2(dppm)Cl_2] and [Au_2(dcpm)Cl_2], respectively, with two equivalents of 4′-sulfanylmonobenzo[15]-crown-5 in the presence of triethylamine in dichloromethane under an inert atmosphere of nitrogen (dppm = bis(diphenylphosphanyl)methane; dcpm = bis(dicyclohexylphosphanyl)methane). The identities of **1** and **2** were confirmed by ^{1}H NMR spectroscopy, positive-ion FAB-mass spectrometry, and satisfactory elemental analyses,[10] and the structure of **2** was confirmed by an X-ray crystal structure determination; the Au–Au separation is 3.28 Å.[11]



1, R = phenyl
2, R = cyclohexyl

The electronic spectra of **1** and **2** in dichloromethane/methanol (1/1) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte show spectral changes upon addition of K$^+$ ions (Figure 1). Isosbestic points were observed at 266, 335, and 390 nm for **1** and at 235 and 352 nm for **2**, which are indicative of a clean reaction. Control experiments with the crown-free analogues [Au_2(dppm){S-3,4-(OMe)$_2C_6H_4$}$_2$] (**3**) and [Au_2(dcpm){S-3,4-(OMe)$_2C_6H_4$}$_2$] (**4**) showed no UV/Vis spectral changes upon addition of K$^+$ ions under the

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