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Syntheses, Structural Characterization, and Host–Guest Chemistry of Ethynylcrown Ether Containing Polynuclear Gold(I) Complexes

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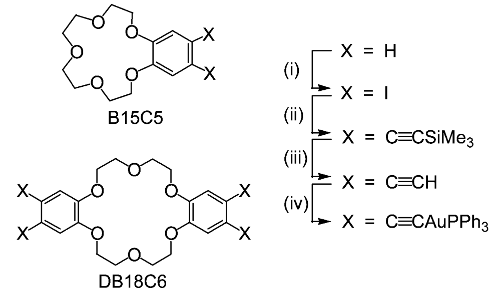
Two novel ethynylcrown ether containing di- and tetranuclear gold(I) complexes have been synthesized and structurally characterized; their binding ability toward various metal ions has also been studied.

The blossoming of gold(I) chemistry in the past few decades has been partially invoked by the presence of its unique aurophilicity and the associated rich photoluminescence properties.[1–3] Recently we reported a series of dinuclear gold(I) mercaptocrown ether containing complexes as luminescence chemosensors toward alkali metal ions.[4] The Au$\cdots$Au interactions and a low-energy emission characteristic of the presence of Au$\cdots$Au interactions were shown to be switched on upon the encapsulation of metal ions of appropriate sizes. With the recent enormous attention focused on the chemistry of carbon-rich organometallics,[5,6] it was thought that the preferred linear two-coordinate geometry and unique aurophilicity of gold(I) centers, together with the sp hybridized carbon-rich alkynyls, could also be employed for the design of luminescent chemosensors. Alkynyls should serve as good candidates for the design of chemosensing systems due to their simple linear geometry and rigidity, in addition to the presence of a conjugated π system which is usually involved in the origin of the luminescence. Herein we report the design and syntheses of a novel class of crown ether ligands of different cavity sizes that possess two and four alkynyl units attached in a branched fashion. Bis- and tetrakis-aurated complexes have also been successfully isolated and structurally characterized, and these, to the best of our knowledge, also represent the only examples of disubstitution of ethynylgold(I) at the ortho positions of the benzene moiety to date. Meta- and para-disubstituted ethynylgold(I) aryls on the other hand are not uncommon.[7] Their binding behavior toward alkali metal ions has also been investigated.

Scheme 1 [a]



[a] Reagents and conditions: (i) ICl, $CHCl_3$; (ii) $HC\equiv CSiMe_3$, Et_3N, $Pd(PPh_3)_2Cl_2$, CuI; (iii) Na_2CO_3, MeOH; (iv) Et_3N, $Au(PPh_3)Cl$, CuI, THF.

4,5-Diethynylbenzo-15-crown-5 $[(HC\equiv C)_2B15C5\text{-}4,5]$ and 4,4′,5,5′-tetraethynyldibenzo-18-crown-6 $[(HC\equiv C)_4DB18C6\text{-}4,4',5,5']$ were obtained by iodination of the respective benzo crowns using ICl in $CHCl_3$, followed by Sonogashira cross-coupling reaction and subsequent desilylation of the trimethylsilylalkynes (Scheme 1).[8] Reaction of $[(HC\equiv C)_2B15C5\text{-}4,5]$ with 2 equiv of $[Au(PPh_3)Cl]$ in the presence of an excess of triethylamine and a catalytic amount of CuI in thf afforded $[\{(Ph_3P)AuC\equiv C\}_2B15C5\text{-}4,5]$ (**1**) as yellow crystals after subsequent recrystallization from dichloromethane−*n*-hexane. $[\{(Ph_3P)AuC\equiv C\}_4DB18C6\text{-}4,4',5,5']$ (**2**) was prepared similarly to **1** except that $[(HC\equiv C)_4DB18C6\text{-}4,4',5,5']$ and 4 equiv of $[Au(PPh_3)Cl]$ were used instead. The identities

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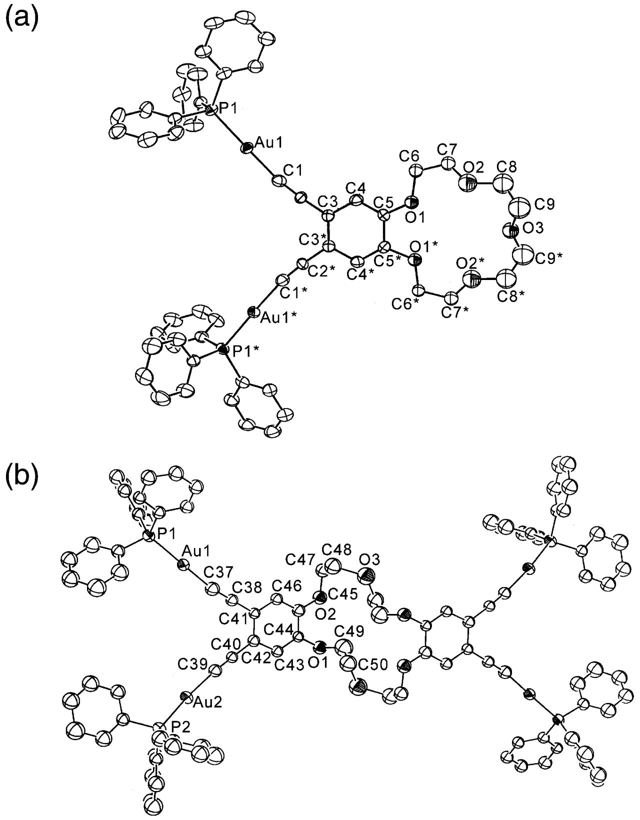

Figure 1. Perspective drawings of (a) $[\{(Ph_3P)AuC{\equiv}C\}_2B15C5\text{-}4,5]$ (**1**) and (b) $[\{(Ph_3)PAuC{\equiv}C\}_4DB18C6\text{-}4,4',5,5']$ (**2**) with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 1. Photophysical Data of Complexes **1** and **2**

complex	absorption λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})^a	medium (T/ K)	emission λ/nm (τ_0/μs)
1	268 (41990)	solid (298)	530 (<0.1)
	276sh (33910)	solid (77)	535 (<0.1)
	320 (22230)	CH_2Cl_2 (298)	530 (1.2)
	334 (22750)	CH_2Cl_2 (77)	500, 538 (4.7)^b
2	268 (68465)	solid (298)	555 (<0.1)
	276sh (56195)	solid (77)	555 (<0.1)
	317 (42280)	CH_2Cl_2 (298)	560 (1.7)
	335 (30150)	CH_2Cl_2 (77)	535 (<0.1)

^{a} Measured in CH_2Cl_2 at 298 K. ^{b} Vibronically structured, with progressional spacings of ca. 1400 cm^{-1}.

of both **1** and **2** have been confirmed by satisfactory elemental analyses, ^{1}H NMR, $^{31}P\{^1H\}$ NMR, IR, and positive FAB-MS. Their solid-state structures have also been determined by X-ray crystallography.

The perspective drawings of **1** and **2** are shown in Figure 1. The molecular structure of **1** is essentially planar except for the two triphenylphosphine units which are arranged in a typical trigonal pyramidal fashion. The angle of 178.9° for C(1)−Au(1)−P(1) is close to linearity and is typical of sp hybridization for the Au(I) and acetylenic carbon. The C≡C bond distance of 1.187(9) Å is also typical of gold(I) alkynyl systems. The shortest Au···Au contact is 7.499 Å, which indicates the absence of both inter- and intramolecular Au···Au interactions. Complex **2** adopts a "chair" conformation with the 4,4′,5,5′-tetraethynyldibenzo-18-crown-6 unit at the center, and linked to the four $Au(PPh_3)$ units via the acetylenic carbons on the two sides of the ethynylcrown ether, with two −P−Au−C≡C− units on the same side of the complex pointing up and the other two pointing down. The two adjacent −P−Au−C≡C− units on the same side of the complex deviate only slightly from coplanarity. The respective P(1)−Au(1)−C(37) and Au(1)−C(41)−C(44) angles of 176.9° and 174.0° are almost linear, with slight deviations from the ideal 180°. All other bond angles and bond lengths are normal and comparable to that of **1**.

Both complexes **1** and **2** exhibit intense absorptions at ca. 268−335 nm with tails extending to ca. 400 nm for the former and ca. 500 nm for the latter (Table 1). The intense absorption bands at 268−276 nm are tentatively assigned to the intraligand transition characteristic of triphenylphosphine, since similar absorption bands are also observed in the mononuclear $[Au(PPh_3)(C{\equiv}CPh)]$ and $[Au(PPh_3)Cl]$.[9,10] The lower energy absorption bands at 317−335 nm are assigned as $\pi \rightarrow \pi^*$ intraligand transitions of the alkynyl ligands. This is supported by the observation of similar bands in the mononuclear $[Au(PPh_3)(C{\equiv}CPh)]$ and $[Au(PPh_3)(C{\equiv}CC_6H_4\text{-}OMe\text{-}p)]$, as well as the dinuclear $[Au_2(dppb)(C{\equiv}CPh)_2]$.[9,10] With reference to the electronic absorption studies of the related alkynylgold(I) phosphine complexes,[9,10] the low energy absorption tails extending to ca. 400−500 nm may be characteristic of the alkynylgold(I) systems. Excitation of solid samples and dichloromethane solutions of **1** and **2** at $\lambda > 350$ nm at both room temperature and 77 K produced long-lived intense luminescence at ca. 530−560 nm. The relatively large Stokes shift together with the observed luminescence lifetimes in the microsecond range are suggestive of emission with triplet parentage. An origin tentatively assigned to states arising from $\sigma(Au-P) \rightarrow \pi^*(C{\equiv}C)$ or metal-perturbed intraligand $\pi \rightarrow \pi^*(C{\equiv}C)$ transition is suggested. In view of the lack of intra- and intermolecular Au···Au interactions, as found in the X-ray crystal structures, the slight red shift of the emission energy from **1** to **2** may be ascribed to the different electronic effects of the tetraynyl versus the di-ynyl ligands.

The change in the UV−vis absorption spectra upon addition of alkali metal ions to a solution of **1** or **2** in CH_2Cl_2−MeOH (1:1 v/v, 0.1 M $^nBu_4NPF_6$) was monitored. Addition of Na^+ to **1** (Figure 2) and K^+ to **2** gave rise to observable UV−vis absorption spectral changes. For instance, clean isosbestic points at 290, 314, and 355 nm for **1** were observed in Figure 2, indicating that the reaction is clean and probably involves only two absorbing species present in equilibrium in the solution. The binding constants (K_s) of the ethynylcrown ether containing complexes for metal ions at 298 K are determined by using the equation derived for a 1:1 complexation stoichiometry.[11,12] The close

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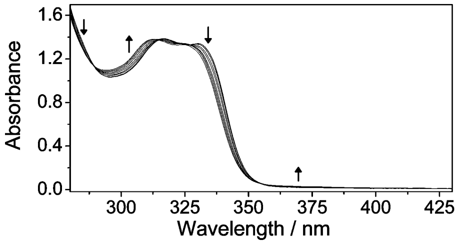

Figure 2. The electronic absorption spectral traces of [{(Ph$_3$P)AuC≡C}$_2$-B15C5-4,5] (**1**) in CH$_2$Cl$_2$−MeOH (1:1 v/v) upon addition of NaClO$_4$ at 298 K.

agreement of the experimental data to the theoretical fits is supportive of a 1:1 complexation stoichiometry. It is found that the log K_s values of **1** for Na$^+$ and **2** for K$^+$ ions are 3.2 and 5.1, respectively. Studies of the binding behavior of **1** toward K$^+$ and **2** toward Cs$^+$ have also been pursued, but only very little spectral changes have been observed, making the determination of the corresponding binding constants unreliable and difficult. Such findings signify the 1:1 binding ability of alkali metal ions toward crown ether moieties of appropriate cavity sizes and suggest the preferential binding of Na$^+$ ions to **1** and K$^+$ to **2**. The ion-binding processes were also investigated by emission spectrophotometric methods, albeit the spectroscopic changes upon addition of ions were too small to be determined. Nevertheless, uptake of alkali metal cations by the crown moieties of **1** and **2** has been further supported by the positive ESI-MS experiments. For **1** and **2**, 1:1 adducts such as [**1**·Na]$^+$ and [**2**·K]$^+$ could be observed.

In summary, two novel crown ethers that are functionalized with two and four ethynyl units have been successfully synthesized. Incorporation of Ph$_3$PAu units to these ligands can give the respective di- and tetranuclear gold(I) complexes, all of which have been structurally characterized and shown to exhibit rich photoluminescence properties. The binding ability toward various metal ions has also been studied. Such a class of complexes may serve as model systems for the design and development of molecular chemosensors as well as for the construction of molecular assemblies and architecture.

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Supporting Information Available: Characterization data of ligands and complexes **1** and **2** and the X-ray crystallographic determination data of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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