ChemComm

Synthesis, structural characterization and binding studies of a novel dinuclear gold(I) calix[4]crown acetylide complex

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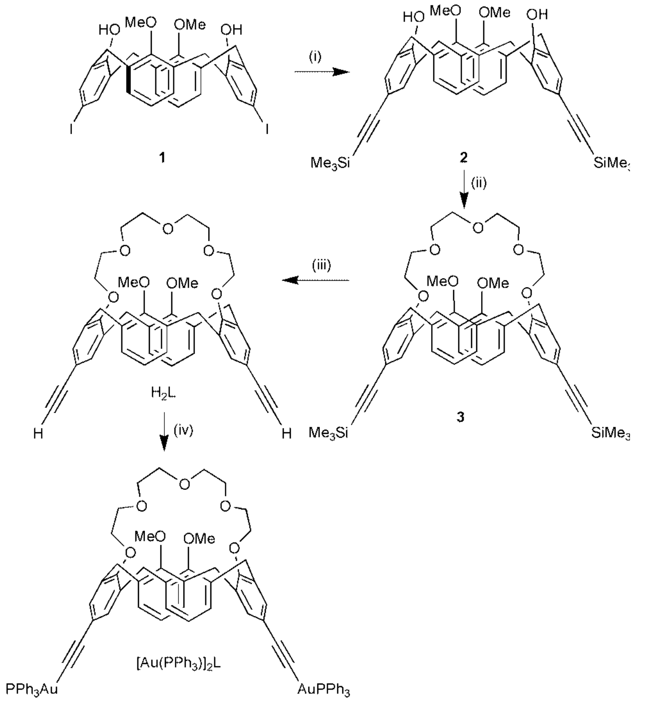
Received (in Cambridge, UK) 3rd May 2000, Accepted 21st June 2000
Published on the Web 24th July 2000

A novel dinuclear gold(I) calix[4]crown acetylide complex, $[Au(PPh_3)]_2L$, has been synthesized and structurally characterized; binding studies of the complex revealed a high K^+/Na^+ selectivity.

During the last decade, there has been a growing interest in the study of calix[*n*]arenes,[1,2] owing to their unique molecular structure and simple one-pot preparation. Indeed, calix[4]arene has proven to be a very important building block in supramolecular chemistry.[3] The easy chemical transformability of this molecule, together with its 'tunable' molecular shape and conformation, makes calix[*n*]arene an attractive candidate for molecular design strategies and has led to an increasing number of examples in the literature. In particular the calix[4]arene is the best developed of the calix[*n*]arene family as a molecular scaffold for the synthesis of more elaborate molecules, supramolecular assemblies, sensors,[4] and receptors.[5]

The recent interest in calixcrowns, which represent a class of calixarenes functionalized with crown ether moieties on the lower rim, together with our recent efforts in the utilization of crown ether-containing metal complexes in the design of selective spectrochemical and luminescence ion probes,[6] have prompted us to extend our work to the calixcrown system. Herein are reported the synthesis, structural characterization, and binding behaviour of a novel dinuclear gold(I) calix[4]-crown acetylide complex.



1

2

3

H_2L

$[Au(PPh_3)]_2L$

Scheme 1 *Reagents and conditions*: (i) $HC{\equiv}CSiMe_3$, Et_3N, $Pd(PPh_3)_2Cl_2$, CuI; (ii) tetraethylene glycol bis(toluene-*p*-sulfonate), Cs_2CO_3, CH_3CN; (iii) KF, DMF, 65 °C; (iv) NaOEt, $(PPh_3)AuCl$, EtOH.

The reaction of (**1**)[7] with (trimethylsilyl)acetylene in the presence of CuI, $Pd(PPh_3)_2Cl_2$ and triethylamine for 24 h at *ca.* 40 °C gave **2** in 50% yield (Scheme 1). Introduction of the polyether linkage into the lower rim was accomplished by reacting **2** with tetraethylene glycol bis(toluene-*p*-sulfonate) in the presence of Cs_2CO_3 in MeCN to give **3**, followed by deprotection of the trimethylsilyl groups by KF to give H_2L in moderate yield. Reaction of $Au(PPh_3)Cl$ with H_2L in the presence of NaOEt in EtOH afforded the desired complex, $[Au(PPh_3)]_2L$, as pale yellow crystals after subsequent recrystallisation using dichloromethane–*n*-hexane. The identities of **2**, **3**, H_2L and $[Au(PPh_3)]_2L$ have been confirmed by satisfactory elemental analyses, ^1H NMR, ^{31}P NMR, IR, and FAB-MS.† The structure of $[Au(PPh_3)]_2L$ has also been determined by X-ray crystallography.‡

Fig. 1 shows $[Au(PPh_3)]_2L$ with atomic numbering. The calix[4]crown in the gold(I) complex shows a cone conformation. Cone conformation is also known in 1,3-calixcrown compounds[8] although a 1,3-alternate conformation[9] is more commonly found. The two gold atoms adopt an essentially linear coordination geometry, with P–Au–C bond angles of

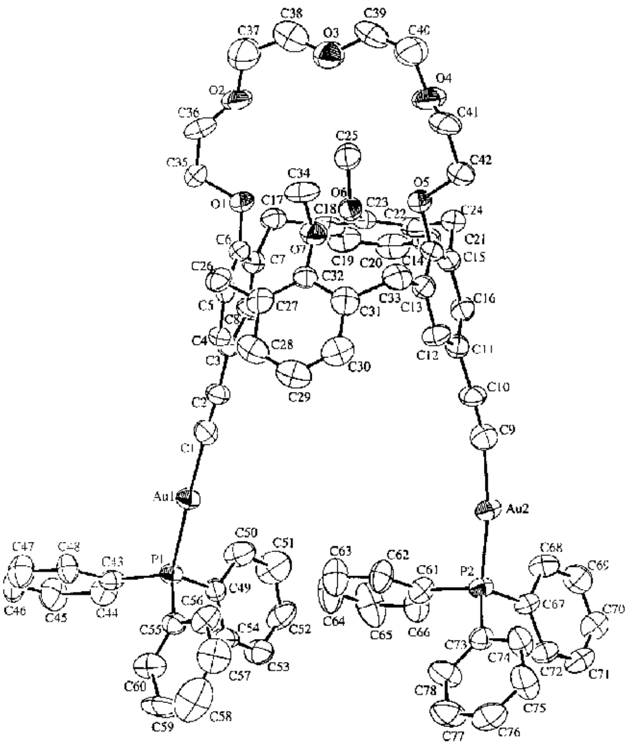


Fig. 1 Perspective drawing of $[Au(PPh_3)]_2L$ with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and bond angles (°): Au(1)–P(1) 2.283(3), Au(2)–P(2) 2.275(3), Au(1)–C(1) 2.04(1), Au(2)–C(9) 2.04(1), C(1)–C(2) 1.18(2), C(9)–C(10) 1.17(2); P(1)–Au(1)–C(1) 177.9(4), P(2)–Au(2)–C(9) 170.5(4), Au(1)–C(1)–C(2) 177(1), Au(2)–C(9)–C(10) 166(1).

DOI: 10.1039/b003536j

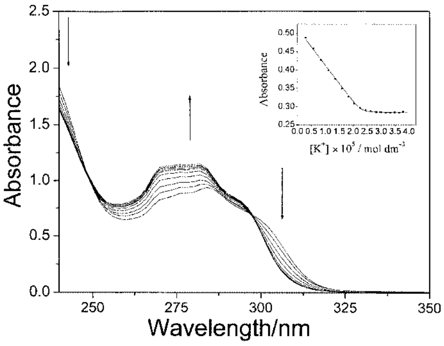


Fig. 2 UV-Vis absorption spectral changes of $[Au(PPh_3)]_2L$ (2×10^{-5} mol dm^{-3}) upon addition of various concentrations of potassium hexafluorophosphate in dichloromethane–methanol (1 : 1 v/v) containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. The insert shows a plot of *A versus* [K$^+$] at 304 nm and its theoretical fit.

170.5(4) and 177.9(4)°; the slight deviation from a perfect 180° is probably a result of the steric demand of the ligands and crystal packing forces. The C≡C bond lengths of 1.18(2) and 1.17(2) Å are typical of terminal Au(I) acetylides.[10,11]

The electronic absorption spectra of $[Au(PPh_3)]_2L$ in dichloromethane–methanol (1 : 1 v/v) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte show spectral changes upon addition of K$^+$ and Na$^+$ ions. Fig. 2 shows the UV-vis spectral traces of $[Au(PPh_3)]_2L$ upon addition of K$^+$ ions. Isosbestic points were observed at 244 and 298 nm which are indicative of a clean reaction. Theoretical fits of the plots of absorbance *vs.* [K$^+$] or [Na$^+$] to eqn. (1) derived for a

$$X = X_o + \frac{X_{\lim} - X_o}{2C_o}[C_o + C_m + 1/K_s - [(C_o + C_m + 1/K_s)^2 - 4C_oC_m]^{\frac{1}{2}}] \quad (1)$$

1 : 1 complexation stoichiometry gave the stability constant K_s. In eqn. (1) X_o, X and $X_{\lim}$ are the initial absorbance of $[Au(PPh_3)]_2L$, the absorbance after the addition of a given amount of salt at concentration C_m, and the limiting absorbance of $[Au(PPh_3)]_2L$ in the fully complexed state, respectively; C_o is the initial concentration of $[Au(PPh_3)]_2L$ and C_m is the total salt concentration. The log K_s values of 7.24 and 2.75 were obtained for the binding of K$^+$ and Na$^+$ ions, respectively. The selective recognition of K$^+$ over Na$^+$ with a K$^+$/Na$^+$ selectivity of 3×10^5, which is higher than a related 1,3-dimethoxycalix[4]arene crown compound (K$^+$/Na$^+$ selectivity = 3×10^3),[9a] and even higher than that of the naturally occurring valinomycin,[12] may suggest that the present complex would serve as a promising candidate for application as a selective K$^+$ ion chemosensor.

V. W.-W. Y. acknowledges financial support from the Research Grants Council and The University of Hong Kong, K.-L. C. the receipt of a postgraduate studentship, and K. M.-C. W. the receipt of a University Post-Doctoral Fellowship, both administered by The University of Hong Kong.

Notes and references

† **2**: ^{1}H NMR (300 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 0.15 (s, 18H, SiMe$_3$), 3.31 (d, 4H, *J* 13.2 Hz, Ar-C*H*$_2$-Ar), 3.88 (s, 6H, OCH$_3$), 4.15 (d, 4H, *J* 13.2 Hz, Ar-C*H*$_2$-Ar), 6.72–7.14 (m, 10H, Ar), 8.03 (s, 2H, OH); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 30.8, 63.7, 91.7, 105.9, 113.3, 125.3, 128.0, 129.3, 132.0, 132.5, 153.0, 154.0; IR (KBr, ν/cm^{-1}): 2957, 2905s ν(C-H$_{\text{aliphatic}}$), 2150m ν(C≡C); positive FAB-MS: ion clusters at *m*/*z* 645 {M$^+$}. Elemental analyses. Found: C 73.73, H 7.16. Calcd. for $C_{40}H_{44}O_4Si_2\cdot\frac{1}{2}H_2O$: C 73.47, H 6.94%. **3**: ^{1}H NMR (300 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 0.14 (s, 18H, SiMe$_3$), 3.16 (d, 4H, *J* 12.4 Hz, Ar-C*H*$_2$-Ar), 3.55–3.90 (m, 16H, OCH$_2$CH$_2$O), 4.10 (s, 6H, OCH$_3$), 4.37 (d, 4H, *J* 12.4 Hz, Ar-C*H*$_2$-Ar), 6.79 (s, 4H, aryl protons *ortho* to C≡C), 6.89 (t, 2H, *J* 7.3 Hz, aryl protons *para* to OCH$_3$), 7.09 (d, 4H, *J* 7.3 Hz, aryl protons *meta* to OCH$_3$); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 31.1, 61.1, 65.8, 70.7, 70.8, 71.4, 123.0, 124.5, 128.7, 132.1, 133.5, 135.6, 156.4, 158.9. IR (KBr, ν/cm^{-1}): 2922, 2903, 2872s ν(C-H$_{\text{aliphatic}}$), 2154m ν(C≡C); positive FAB-MS: ion cluster at *m*/*z* 803 {M$^+$}, 826 {M + Na$^+$}. Elemental analyses. Found: C 71.63, H 7.05. Calcd. for $C_{48}H_{58}O_7Si_2$: C 71.78, H 7.28%. **H$_2$L**: ^{1}H NMR (300 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 2.77 (s, 2H, C≡CH), 3.16 (d, 4H, *J* 12.6 Hz, Ar-C*H*$_2$-Ar), 3.56–3.93 (m, 16H, OCH$_2$CH$_2$O), 4.10 (s, 6H, OCH$_3$), 4.38 (d, 4H, *J* 12.6 Hz, Ar-C*H*$_2$-Ar), 6.76 (s, 4H, aryl protons *ortho* to C≡C), 6.88 (t, 2H, *J* 7.3 Hz, aryl protons *para* to OCH$_3$), 7.08 (d, 4H, *J* 7.3 Hz, aryl protons *meta* to OCH$_3$); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 31.1, 61.2, 70.8, 70.9, 71.5, 73.4, 75.4, 84.32, 115.9, 123.1, 128.7, 132.1, 133.8, 156.4, 158.9; IR (KBr, ν/cm^{-1}): 3292s ν(≡CH), 2909, 2868s ν(C-H$_{\text{aliphatic}}$), 2107w ν(C≡C); positive FAB-MS: ion cluster at *m*/*z* 658 {M$^+$}, 681 {M + Na$^+$}. Elemental analyses. Found: C 72.86, H 6.24. Calcd. for $C_{42}H_{42}O_7\cdot\frac{1}{2}CH_2Cl_2$: C 72.79, H 6.18%. $[Au(PPh_3)]_2L$: ^{1}H NMR (300 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 3.12 (d, 4H, *J* 12.6 Hz, Ar-C*H*$_2$-Ar), 3.65–4.00 (m, 16H, OCH$_2$CH$_2$O), 4.05 (s, 6H, OCH$_3$), 4.32 (d, 4H, *J* 12.6 Hz, Ar-C*H*$_2$-Ar), 6.55–7.10 (m, 10H, Ar), 7.25–7.58 (m, 30H, PPh$_3$); ^{31}P NMR (202 MHz, CDCl$_3$, 298 K, relative to 85% H$_3$PO$_4$): δ 43.5 (s, PPh$_3$); IR (KBr, ν/cm^{-1}): 2918, 2866s ν(C-H$_{\text{aliphatic}}$), 2099w ν(C≡C); positive FAB-MS: ion cluster at *m*/*z* 1597 {M + Na$^+$}; UV-Vis [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: CH$_2$Cl$_2$, 276 (44440), 286 (48930), 306 sh (31050), 344 (11370). Elemental analyses. Found: C 59.54, H 4.72. Calcd. for $C_{78}H_{70}O_7Au_2P_2$: C 59.47, H 4.48%.

‡ *Crystal data* for $[Au(PPh_3)]_2L$: $[C_{78}H_{70}O_7P_2Au_2.H_2O]$, M_r = 1593.30, triclinic, space group $P1$ (No. 2), a = 13.108(2), b = 15.195(2), c = 21.461(3) Å, α = 83.57(2), β = 76.71(2), γ = 65.43(2)°, V = 3782(1) Å^3, Z = 2, D_c = 1.399 g cm^{-3}, μ(Mo-Kα) = 39.80 cm^{-1}, F(000) = 1584, T = 301 K. A crystallographic asymmetric unit consists of one formula unit. Convergence for 806 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ for 7855 reflections with $I > 3\sigma(I)$ was reached at R = 0.055 and wR = 0.081 with a goodness-of-fit of 2.16. CCDC 182/1705. See http://www.rsc.org/suppdata/cc/b0/b003536j/ for crystallographic files in .cif format. X-Ray crystallographic data is available as supplementary data available from BLDSC (suppl. no. 57711, pp. 25) or the RSC library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

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