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Design, Synthesis, Photophysics, and Ion-binding Studies of a Ditopic Receptor Based on Gold(I) Phosphine Thiolate Complex Functionalized with Crown Ether and Urea Binding Units

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A ditopic receptor based on gold(I) phosphine thiolate complex [(B15C5Ph$_2$P)Au(SC$_6$H$_4$NHCONHC$_6$H$_5$)] (**1**) together with a related crown-free analogue, [(Ph$_3$P)Au(SC$_6$H$_4$NHCONHC$_6$H$_5$)] (**2**), have been designed and synthesized and their photophysical properties studied. Complex **1** featured both a benzo-15-crown-5 cation-binding unit in the auxiliary phosphine ligand and a urea-functionalized thiolate as an anion receptor moiety. The anion- and cation-binding study, salt extraction ability, as well as the cooperativity have been studied using ^{1}H NMR and ESI-MS techniques.

Introduction

Since Pedersen's discovery of crown ethers in 1967,[1a] supramolecular host−guest chemistry has attracted much attention that goes beyond the complexation of cations to more comprehensive views that include anion sensing.[1−3] Recently, much effort on the development of a heteroditopic receptor, which incorporates both individual cation- and anion-binding sites within a single molecule, has been driven by its great potential applications, such as in efficient extraction and as a carrier transportation reagent for environmentally important ion-pair species.[4−8] The ditopic hosts are expected to exhibit allosteric and cooperative effects, where the binding of one ion alters the association affinity of the counterion through electrostatic and conformational effects. The ion-pair recognition can also play an important role in controlling the geometry in supramolecular chemistry. Most of the studies on the heteroditopic hosts have focused on the organic molecules.[4] There has also been increasing interest in the use of inorganic and organometallic transition metal complexes as chemosensors for cations and anions, due to the diversity of their geometry, redox activity, and rich photophysical properties.[3,9,10] However, ion-pair receptors based on metal complexes have been relatively much less explored.[11]

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(1) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017. (b) Pedersen, C. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1021. (c) Cram, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1009. (d) Lehn, J. M. *Angew. Chem., Int. Ed.* **1988**, *27*, 89. (e) Lehn, J. M. *Science* **2002**, *295*, 2400.

(2) (a) Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, U. K., 2006. (b) Martínez-Mánez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (c) Wiskup, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res.* **2001**, *34*, 963.

(3) (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (b) Steed, J. W. *Chem. Soc. Rev.* **2009**, *38*, 506. (c) Caltagirone, C.; Gale, P. A. *Chem. Soc. Rev.* **2009**, *38*, 520.

(4) (a) Reetz, M. T.; Niemeyer, C. M.; Harms, K. *Angew. Chem., Int. Ed.* **1991**, *30*, 1474. (b) White, D. J.; Laing, N.; Miller, H.; Parsons, S.; Coles, S.; Tasker, P. A. *Chem. Commun.* **1999**, 2077. (c) Shi, X.; Fettinger, J. C.; Davis, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2827. (d) Turner, D. R.; Spencer, E. C.; Howard, J. A. K.; Tocherb, D. A.; Steed, J. W. *Chem. Commun.* **2004**, 1352. (e) Domenico, G.; Giuseppe, G.; Anna, N.; Andrea, P.; Sebastiano, P.; Melchiorre, F. P.; Marta, P.; Ilenia, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 4892. (f) Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissanen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3641.

(5) (a) Mahoney, J. M.; Stucker, K. A.; Jiang, H.; Carmichael, I.; Brinkmann, N. R.; Beatty, A. M.; Noll, B. C.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 2922. (b) Deetz, M. J.; Shang, M.; Smith, B. D. *J. Am. Chem. Soc.* **2000**, *122*, 6201. (c) Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 7617. (d) Shukla, R.; Kida, T.; Smith, B. D. *Org. Lett.* **2000**, *2*, 3099.

(6) (a) Wintergerst, M. P.; Levitskaia, T. G.; Moyer, B. A.; Sessler, J. L.; Delmau, L. H. *J. Am. Chem. Soc.* **2008**, *130*, 4129. (b) Sessler, J. L.; Kim, S. K.; Gross, D. E.; Lee, C.-H.; Kim, J. S.; Lynch, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 13162.

(7) (a) Niikura, K.; Anslyn, E. V. *J. Org. Chem.* **2003**, *68*, 10156. (b) Tobey, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 10963. (c) Tobey, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 14807.

(8) (a) Lankshear, M. D.; Dudley, I. M.; Chan, K.-M.; Beer, P. D. *New J. Chem.* **2007**, *31*, 684. (b) Beer, P. D.; Hopkins, P. K.; McKinney, J. D. *Chem. Commun.* **1999**, 1253. (c) Lankshear, M. D.; Dudley, I. M.; Chan, K.-M.; Cowley, A. R.; Santos, S. M.; Felix, V.; Beer, P. D. *Chem.—Eur. J.* **2008**, *14*, 2248.

(9) (a) Balzani, V.; Sabbatina, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319. (b) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108. (c) Shen, Y.; Sullivan, B. P. *Inorg. Chem.* **1995**, *34*, 6235. (d) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71.

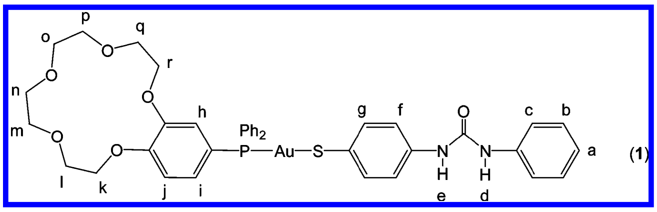
(10) (a) Li, M. J.; Chu, B. W. K.; Yam, V. W. W. *Chem.—Eur. J.* **2006**, *12*, 3528. (b) Li, M. J.; Ko, C. C.; Duan, G. P.; Zhu, N.; Yam, V. W. W. *Organometallics* **2007**, *26*, 6091. (c) Tang, W. S.; Lu, X. X.; Wong, K. M. C.; Yam, V. W. W. *J. Mater. Chem.* **2005**, *15*, 2714.

(11) Miyaji, H.; Collnson, S. R.; Prokeŝ, I.; Tucker, J. H. R. *Chem. Commun.* **2003**, 64.

Gold(I) chemistry has been the subject of extensive study due to its wide range of potential applications, such as in biological activity,[12] catalysis,[13] and surface technology.[14] Intriguing luminescence and interesting supramolecular structures are also prominent properties. The presence of Au···Au interactions[15] has been shown to play an important role in governing the unique electronic absorption and emission features in these complexes[16] but also is believed to be responsible for the construction of a wide range of fascinating supramolecular architectures.[17] A number of luminescent mono-, di-, and polynuclear gold(I) complexes have been reported,[16−25] many of which show fascinating supramolecular structures as a result of Au···Au interactions.[16−25]

On the basis of our interest in the study of luminescent gold(I) complexes and their supramolecular and host−guest chemistry, a number of homotopic receptors based on gold(I) complexes, such as di- and tetranuclear gold(I) alkynylcrown[18] and alkynylcalixcrown complexes,[17] which have been shown to exhibit interesting photophysical and cation-binding properties, have been reported. Recently, a novel dipicolylamine-containing alkynylgold(I) complex has been successfully synthesized and structurally characterized, which has been shown to exhibit rich photoluminescence properties and to function as a selective sensor for Cu^{2+}, as revealed by the large UV−vis change and significant emission quenching.[20] In addition, the utilization of the switching on and off of Au···Au interactions has been successfully demonstrated as a novel strategy of optical signal transduction for chemosensing.[21−23]

Given the two-coordinate nature of gold(I) complexes, the rich photophysical properties, as well as the good affinity of gold(I) to a variety of ligands, it is envisaged that a gold(I) complex would provide an ideal platform to construct ditopic receptors. As an extension of our previous work on host−guest chemistry, herein are reported the design and synthesis of a simple but novel ditopic receptor based on the gold(I) phosphine thiolate complex $[(B15C5Ph_2P)Au(SC_6H_4NHCONHC_6H_5)]$ (**1**), together with its related crown-free analogue $[(Ph_3P)Au(SC_6H_4NHCONHC_6H_5)]$ (**2**), and the study of their photophysical properties. Complex **1** featured both a benzo-15-crown-5 cation-binding unit in the auxiliary phosphine ligand and a urea-functionalized thiolate as an anion receptor moiety. With such a design, it is envisaged that complex **1** could bind both cations and anions simultaneously. The anion- and cation-binding properties, salt extraction ability, and the cooperativity have also been studied using ^1H NMR and ESI-MS techniques.



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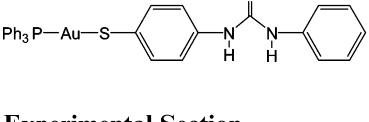

(2)

Experimental Section

Materials and Reagents. Potassium tetrachloroaurate(III) and triphenylphosphine were purchased from Strem Chemicals Inc. 2,2′-Thiodiethanol, chlorodiphenylphosphine, lithium aluminum hydride, phenyl isocyanate, and tetra-*n*-butylammonium hexafluorophosphate were purchased from Aldrich Chemical Co., and the latter was recrystallized three times from hot absolute ethanol and dried under a vacuum for 12 h prior to use. Tetra-*n*-butylammonium chloride, tetra-*n*-butylammonium

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[12] (a) Hill, D. T.; Sutton, B. M. *Cryst. Struct. Commun* **1980**, *9*, 679. (b) Sutton, B. M.; McGusty, E.; Ealz, D. T.; DiMartino, M. J. *J. Med. Chem.* **1972**, *15*, 1095.

[13] (a) Bond, G. C.; Louis, C.; Thompson, D. T. *Catalysis by Gold*; Imperial College Press: London, 2006. (b) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266.

[14] Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

[15] (a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391. (b) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3. (c) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412. (d) Pyykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed.* **1991**, *30*, 604. (e) McCleskey, T. M.; Gray, H. B. *Inorg . Chem.* **1992**, *31*, 1733. (f) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed.* **1997**, *36*, 1179.

[16] (a) Yam, V. W. W.; Cheng, E. C. C. *Chem. Soc. Rev.* **2008**, *37*, 1806. (b) Yam, V. W. W.; Cheng, E. C. C. *Top. Curr. Chem.* **2007**, *281*, 269.

[17] (a) Yu, S. Y.; Zhang, Z. X.; Cheng, E. C. C.; Li, Y. Z.; Yam, V. W. W.; Huang, H. P.; Zhang, R. *J. Am. Chem. Soc.* **2005**, *127*, 17994. (b) Yu, S. Y.; Sun, Q. F.; Lee, T. K. M.; Cheung, E. C. C.; Li, Y. Z.; Yam, V. W. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 4551. (c) Sun, Q. F.; Lee, T. K. M.; Li, P. Z.; Yao, L. Y.; Huang, J. J.; Huang, J.; Yu, S. Y.; Li, Y. Z.; Cheng, E. C. C.; Yam, V. W. W. *Chem. Commun.* **2008**, 5514.

[18] Lu, X. X.; Li, C. K.; Cheng, E. C. C.; Zhu, N.; Yam, V. W. W. *Inorg. Chem.* **2004**, *43*, 2225.

[19] (a) Yip, S. K.; Cheng, E. C. C.; Yuan, L. H.; Zhou, N.; Yam, V. W. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4954. (b) Yam, V. W. W.; Cheung, K. L.; Yuan, L. H.; Wong, K. M. C.; Cheung, K. K. *Chem. Comm.* **2000**, 1513. (c) Yam, V. W. W.; Yip, S. K.; Yuan, L. H.; Cheung, K. L.; Zhou, N.; Cheung, K. K. *Organometallics* **2003**, *22*, 2630.

[20] He, X.; Zhu, N.; Yam, V. W. W. *Organometallics* **2009**, *28*, 3621.

[21] (a) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323. (b) Yam, V. W. W.; Chan, C. L.; Li, C. K.; Wong, K. M. C. *Coord. Chem. Rev.* **2001**, *216−217*, 173. (c) Yam, V. W. W.; Li, C. K.; Chan, C. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2857. (d) Li, C. K.; Lu, X. X.; Wong, K. M. C.; Chan, C. L.; Zhu, N.; Yam, V. W. W. *Inorg. Chem.* **2004**, *43*, 7421.

[22] He, X.; Lam, W. H.; Zhu, N.; Yam, V. W. W. *Chem.—Eur. J.* **2009**, *15*, 8842.

[23] He, X.; Cheng, E. C. C.; Zhu, N.; Yam, V. W. W. *Chem. Commun.* **2009**, 4016.

[24] Gold(I) alkynyl complexes: (a) Koshevoy, I. O.; Koshinen, L.; Haukka, M.; Tunik, S. P.; Serdobintsev, P. Y.; Melnikov, A. S.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3942. (b) Wei, Q. H.; Zhang, L. Y.; Yin, G. Q.; Shi, L. X.; Chen, Z. N. *J. Am. Chem. Soc.* **2004**, *126*, 9940. (c) Li, D.; Hong, X.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929. (d) Che, C. M.; Chao, H. Y.; Miskowski, V. M.; Li, Y.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 4985. (e) Mingos, D. M. P.; Yan, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1894. (f) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *216−217*, 313. (g) McArdle, C. P.; Van, S.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3959. (h) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 995. (i) Abu-Salah, O. M.; Al-Ohaly, A.; Knobler, C. B. *J. Chem. Soc., Chem.Commun.* **1985**, 1502. (j) de la Riva, H.; Nieuwhuyzen, M.; Fierro, C. M.; Raithby, P. R.; Male, L.; Lagunas, M. C. *Inorg. Chem.* **2006**, *45*, 1418.

[25] Gold(I) thiolate complexes: (a) Vogler, A.; Kunkely, H. *Chem. Phys. Lett.* **1988**, *150*, 135. (b) Bardaji, M.; Laguna, A.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2000**, *39*, 3560. (c) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329. (d) Lee, Y. A.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2002**, *124*, 10662. (e) Lee, Y. A.; Eisenberg, R. *J. Am. Chem. Soc.* **2003**, *125*, 7778. (f) Forward, J. M.; Bohmann, D.; Fackler, J. P., Jr.; Staples, R. J. *Inorg. Chem.* **1995**, *34*, 6330. (g) van Zyl, W. E.; López-de-Luzuriaga, J. M.; Mohamed, A. A.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 4579. (h) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1995**, 745. (i) Jones, W. B.; Yuan, J.; Narayanaswamy, R.; Young, M. A.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1995**, *34*, 1996. (j) Chiari, B.; Piovewsana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 366. (k) Guy, J. J.; Jones, P. G.; Mays, M. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 8. (l) Hanna, S. D.; Khan, S. I.; Zink, J. I. *Inorg. Chem.* **1996**, *35*, 5813. (m) Tang, S. S.; Chang, C. P.; Lin, I. J. B.; Liou, L. S.; Wang, J. C. *Inorg. Chem.* **1997**, *36*, 2294.

bromide, and tetra-*n*-butylammonium iodide were purchased from Fluka. 4-Aminophenyl disulfide,[26] 4′-diphenylphosphino-benzo-15-crown-5 (Ph$_2$P−B15C5),[27] and the gold thiolate polymer [Au-SR]$_\infty$[28] were synthesized according to modified procedures. Dichloromethane, tetrahydrofuran, diethyl ether, and methanol were purified using standard procedures before use.[29] All other reagents were of analytical grade and were used as received. All reactions were carried out under strictly anhydrous and anaerobic conditions using standard Schlenk techniques under an inert atmosphere of nitrogen.

Synthesis. **[C$_6$H$_5$NHCONHC$_6$H$_4$-4-S-]$_2$.** To a solution of 4-aminophenyl disulfide (0.62 g, 2.5 mmol) in anhydrous CH$_2$Cl$_2$ (40 mL) was slowly added phenyl isocyanate (0.6 g, 5.0 mmol) in CH$_2$Cl$_2$ (10 mL) over 10 min, and the mixture was heated to reflux overnight under a nitrogen atmosphere. The precipitate was collected by filtration and washed twice with CH$_2$Cl$_2$ to yield the product as a white solid. Yield: 1.1 g, 91%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K, relative to Me$_4$Si): δ 6.97 (t, *J* = 7.6 Hz, 2 H; −C$_6$H$_5$), 7.27 (t, *J* = 7.6 Hz, 4 H; −C$_6$H$_5$), 7.45 (m, 12 H; −C$_6$H$_5$ and −SC$_6$H$_4$−), 8.73 (s, 2 H; −NH), 8.86 (s, 2 H; −NH). Positive-ion FAB-MS: *m*/*z* 487 [M + 1]$^+$. Elem anal. found (%): C, 62.82; H, 5.15; N, 11.00. Calcd. for C$_{26}$H$_{22}$N$_4$O$_2$S$_2$·CH$_3$OH: C, 62.53; H, 5.05; N, 10.80.

HSC$_6$H$_4$NHCONHC$_6$H$_5$. To a suspension of [C$_6$H$_5$NHCONHC$_6$H$_4$-4-S-]$_2$ (0.8 g, 1.65 mmol) and triphenylphosphine (0.45 g, 1.72 mmol) in a dioxane−water mixture (17:3 v/v, 40 mL) was added 5 drops of concentrated HCl, and the mixture was allowed to stir overnight at 60 °C in a nitrogen atmosphere. The solvent was evaporated under reduced pressure, and the residue was dissolved in an aqueous NaOH solution (5%, 20 mL) and washed with diethyl ether three times. To the aqueous layer collected was added HCl (10%, 20 mL) to precipitate out the desired product, which was filtered and washed with water. Subsequent drying gave the product as a white solid. Yield: 0.5 g, 62%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K, relative to Me$_4$Si): δ 5.17 (s, 1 H; −SH), 6.96 (t, *J* = 7.6 Hz, 1 H; −C$_6$H$_5$), 7.21 (d, *J* = 8.4 Hz, 2 H; −SC$_6$H$_4$−), 7.27 (t, *J* = 7.6 Hz, 2 H; −C$_6$H$_5$), 7.35 (d, *J* = 8.4 Hz, 2 H; −SC$_6$H$_4$−), 7.43 (d, *J* = 8.0 Hz, 2 H; −C$_6$H$_5$), 8.63 (s, 2 H; −NH). Positive ESI-MS: *m*/*z* 244 [M]$^+$. Elem anal. found (%): C, 64.05; H, 4.95; N, 11.54. Calcd. for C$_{13}$H$_{12}$N$_2$OS: C, 63.91; H, 4.95; N, 11.47.

[Au(SC$_6$H$_4$NHCONHC$_6$H$_5$)]$_\infty$. To the solution of KAuCl$_4$ (189 mg, 0.5 mmol) in CH$_3$OH (15 mL) and water (1 mL) was added dropwise 2,2′-thiodiethanol (0.5 mL). The stirring was maintained until the solution turned colorless. HSC$_6$H$_4$NHCONHC$_6$H$_5$ (122 mg, 0.5 mmol) in THF (2 mL) was added, and a white precipitate began to form immediately from the reaction mixture. After stirring for 30 min, the solid was separated; washed with water, CH$_3$OH, and diethyl ether; and dried under a vacuum to give the product as a white solid. Yield: 215 mg, 98%. Elem anal. found (%): C, 35.61; H, 2.77; N, 6.33. Calcd. for C$_{13}$H$_{11}$AuN$_2$OS: C, 35.46; H, 2.52; N, 6.36.

[(B15C5Ph$_2$P)Au(SC$_6$H$_4$NHCONHC$_6$H$_5$)] (1). A mixture of [Au{SC$_6$H$_4$NHCONHC$_6$H$_5$}]$_\infty$ polymer (100 mg, 0.23 mmol) and PPh$_2$B15C5 (103 mg, 0.23 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred for 2 h under N$_2$. The mixture was then filtered, and the solvent was removed under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ and was recrystallized by layering *n*-hexane onto a CH$_2$Cl$_2$ solution of the product and washed with diethyl ether to give **1** as a white solid. Yield: 134 mg, 65%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K, relative to Me$_4$Si): δ 3.60 (m, 8 H; −OCH$_2$−), 3.72 (t, *J* = 4.0 Hz, 2 H; −OCH$_2$−), 3.77 (m, 2 H; −OCH$_2$−), 3.93 (t, *J* = 4.0 Hz, 2 H; −OCH$_2$−), 4.09 (m, 2 H; −OCH$_2$−), 6.95 (t, *J* = 7.3 Hz, 1 H; −C$_6$H$_5$), 7.02 (dd, *J* = 8.4 and 2.4 Hz, 1 H; −C$_6$H$_3$−), 7.10 (dd, *J* = 13.3 and 1.8 Hz, 1 H; −C$_6$H$_3$−), 7.15 (dd, *J* = 8.4 and 2.4 Hz, 1 H; −C$_6$H$_3$−), 7.20 (d, *J* = 8.6 Hz, 2 H; −SC$_6$H$_4$−), 7.26 (t, *J* = 7.6 Hz, 2 H; −C$_6$H$_5$), 7.33 (d, *J* = 8.6 Hz, 2 H; −SC$_6$H$_4$−), 7.43 (d, *J* = 8.5 Hz, 2 H; −C$_6$H$_5$), 7.50−7.62 (m, 10 H; PPh$_2$), 8.48 (s, 1 H; −NH), 8.59 (s, 1 H; −NH). ^{31}P NMR (202 MHz, *d*$_6$-DMSO, relative to 85% H$_3$PO$_4$): δ 38.2. FAB-MS: *m*/*z* 892 [M]$^+$, 649 [M − L]$^+$, 1101 [B15C5Ph$_2$P−Au−PPh$_2$B15C5]$^+$. Elem anal. found (%): C, 53.41; H, 5.16; N, 2.96. Calcd. for C$_{39}$H$_{40}$AuN$_2$O$_6$PS·C$_4$H$_{10}$O: C, 53.42; H, 5.21; N, 2.90.

[(Ph$_3$P)Au(SC$_6$H$_4$NHCONHC$_6$H$_5$)] (2). This was synthesized according to a procedure similar to that of **1** except PPh$_3$ (60 mg, 0.23 mmol) was used in place of PPh$_2$B15C5. Subsequent recrystallization by the diffusion of diethyl ether vapor into a dichloromethane solution of the product gave **2** as a pale yellow solid. Yield: 128 mg, 80%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K, relative to Me$_4$Si): δ 6.95 (t, *J* = 7.3 Hz, 1 H; −C$_6$H$_5$), 7.20 (d, *J* = 8.5 Hz, 2 H; −SC$_6$H$_4$−), 7.26 (t, *J* = 7.7 Hz, 2 H; −C$_6$H$_5$), 7.31 (d, *J* = 8.5 Hz, 2 H; −SC$_6$H$_4$−), 7.42 (d, *J* = 7.7 Hz, 2 H; −C$_6$H$_5$), 7.54−7.64 (m, 15 H; PPh$_3$), 8.46 (s, 1 H; −NH), 8.57 (s, 1 H; −NH). ^{31}P NMR (202 MHz, *d*$_6$-DMSO, relative to 85% H$_3$PO$_4$): δ 38.3. Positive-ion FAB-MS: *m*/*z* 459 [M − L]$^+$, 702 [M]$^+$. Elem anal. found (%): C, 53.48; H, 4.05; N, 3.93. Calcd. for C$_{31}$H$_{26}$AuN$_2$OPS·0.5C$_4$H$_{10}$O: C, 53.59; H, 4.22; N, 3.79.

Physical Measurements and Instrumentation. The UV−vis spectra were recorded on a Hewlett-Packard 8452 A diode array spectrophotometer. ^{1}H NMR spectra with chemical shifts relative to tetramethylsilane (Me$_4$Si) were recorded on a Bruker Avance 400 FT-NMR spectrometer. Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Positive electrospray-ionization (ESI) mass spectra were obtained on a Finnigan LCQ mass spectrometer. Elemental analysis of the new complexes was performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing.

Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. All solutions for photophysical studies were prepared under a high vacuum in a 10-cm^3 round-bottomed flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere with a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze−pump−thaw cycles. Solid-state photophysical measurements were carried out with the solid sample loaded in a quartz tube inside a quartz-walled Dewar flask. Measurements of the ethanol−methanol−dichloromethane (4:1:1, v/v) glass or solid samples at 77 K were conducted by using liquid nitrogen filled in the optical Dewar flask. Excited-state lifetimes of samples in fluid solutions or in the solid states were measured using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620 A (500 MHz, 2 GS s^{-1}) digital oscilloscope, and analyzed by using a program for exponential fits. The concentrations of the gold complexes employed in the UV−vis and emission spectral studies are typically in the range of 2.5×10^{-5} to 2.0×10^{-4} mol dm^{-3}.

Results and Discussion

Synthesis and Characterization. The synthetic route of complexes **1** and **2** is summarized in Scheme 1. 4-Aminophenyl disulfide was first allowed to react with isocyanate

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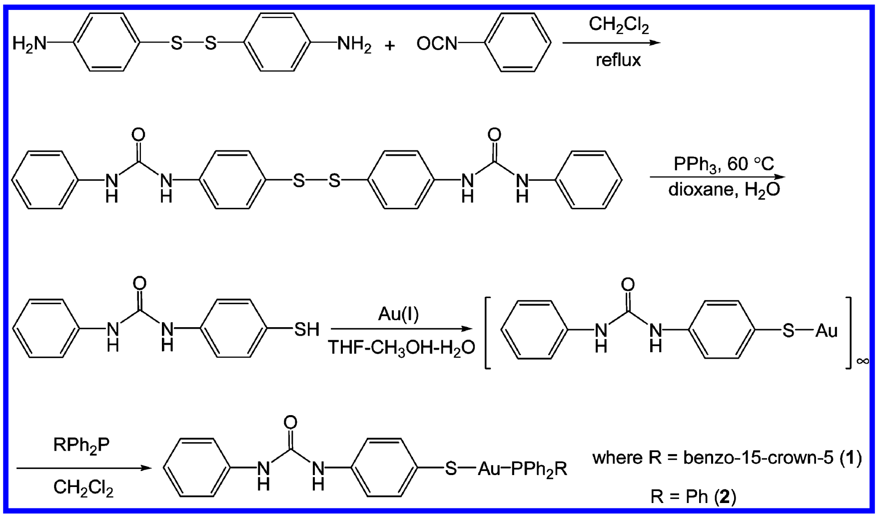
(26) Price, C. C.; Stacy, G. W. *Organic Syntheses*, **1955**, *3*, 86.

(27) Okano, T.; Iwahara, M.; Konishi, H.; Kiji, J. *J. Organomet. Chem.* **1988**, *346*, 267.

(28) Antonella, B.; Oliver, B.; Pietro, D.; Serena, L.; Fabio, M.; Piero, Z. *Eur. J. Inorg. Chem.* **2007**, 865.

(29) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U. K., 1988.

Scheme 1. Synthetic Route of Complexes **1**−**2**



to give the corresponding urea disulfide. This was followed by reduction of the disulfide with triphenylphosphine to give the desired air- and moisture-stable urea-containing thiol in relatively high yield.

The gold(I) phosphine thiolate complexes with a urea receptor were prepared by the reaction of the gold(I) thiolate polymer with the different phosphine ligands. All the newly synthesized complexes have been characterized by ^{1}H NMR, ^{31}P NMR, FAB-MS or ESI-MS, and gave satisfactory elemental analyses. In the positive FAB-mass spectra, besides the parent molecular ion peak $[M]^+$, the $[M - L]^+$ ion cluster which corresponded to the loss of one urea-containing thiolate ligand has always been observed. For complex **1**, the ion cluster due to $[Au(PR_3)_2]^+$ was also present in the spectra with significant intensity.

Electronic Absorption and Emission Properties. The electronic absorption spectra of complexes **1** and **2** show intense high-energy absorption bands at ca. 288−290 nm, with lower-energy tails extending to ca. 400 nm in CH_2Cl_2. The photophysical data are tabulated in Table 1. According to the previous studies on the related phosphinogold(I) thiolate systems,[25] the high-energy absorption bands are tentatively assigned as the intraligand transitions of the phosphine and urea-functionalized thiolate ligands. The low-energy tail, which is absent in the spectra of the corresponding phosphinogold(I) chloride and free ligand, is characteristic of the phosphinogold(I) thiolate systems and is tentatively assigned to the thiolate-to-gold ligand-to-metal charge transfer (LMCT) transition.

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

complex	absorption[a] λ/nm ($\varepsilon \times 10^{-4}$/dm^3 mol^{-1} cm^{-1})	medium (T/K)	emission λ_{em}/nm (τ_0/μs)
1	288 (3.12)	DCM (298)	451, 530 (< 0.1)
		solid (298)	530 (0.5)
		solid (77)	511 (15.0, 3.4)
		glass[b] (77)	451 (70.6, 17.6)
2	290 (2.35)	DCM (298)	426, 534 (0.1, 0.34)
		solid (298)	573 (0.64, 0.1)
		solid (77)	535 (13.4)
		glass[b] (77)	530 (20.2)

[a] In dichloromethane solution. [b] In EtOH−MeOH−CH_2Cl_2 (4:1:1, v/v).

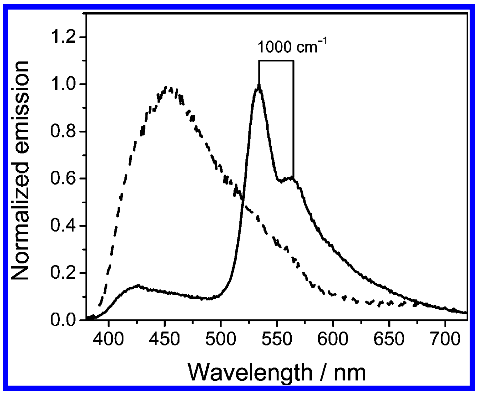


Figure 1. Normalized emission spectra of **1** (----) and **2** (—) in dichloromethane at 298 K.

Excitation of complex **2** in degassed CH_2Cl_2 solution at room temperature gives rise to intense long-lived low-energy emission at ca. 534 nm, with a shoulder at 564 nm, with vibrational progressional spacings of ca. 1000 cm^{-1}, which are tentatively ascribed to the vibrational mode of the N−C−N group on the urea moiety and/or the aromatic C−H deformation modes. A high-energy emission band at ca. 426 nm is also obvious, but with a lower intensity. Unlike its crown-free analogue **2**, excitation of complex **1** in a degassed dichloromethane solution produces an intense high-energy emission at ca. 451 nm, with a low-energy emission shoulder at ca. 530 nm. Figure 1 shows the emission spectra of **1** and **2** in dichloromethane at 298 K. With reference to previous spectroscopic work on gold(I) phosphine thiolate complexes,[25] the lower energy emissions with lifetime in the microsecond range are tentatively assigned as originating from a thiolate-to-gold ligand-to-metal charge transfer (LMCT) excited state of phosphorescence nature. The high-energy emission, which has a lifetime in the nanosecond regime, is tentatively assigned to states arising from the metal-perturbed intraligand transition of fluorescence nature. The relatively weak low-energy emission of complex **1** might be due to the photoinduced electron transfer (PET) quenching effect of the electron-donating oligoether oxygen atoms on the crown ether moiety, as is commonly observed in

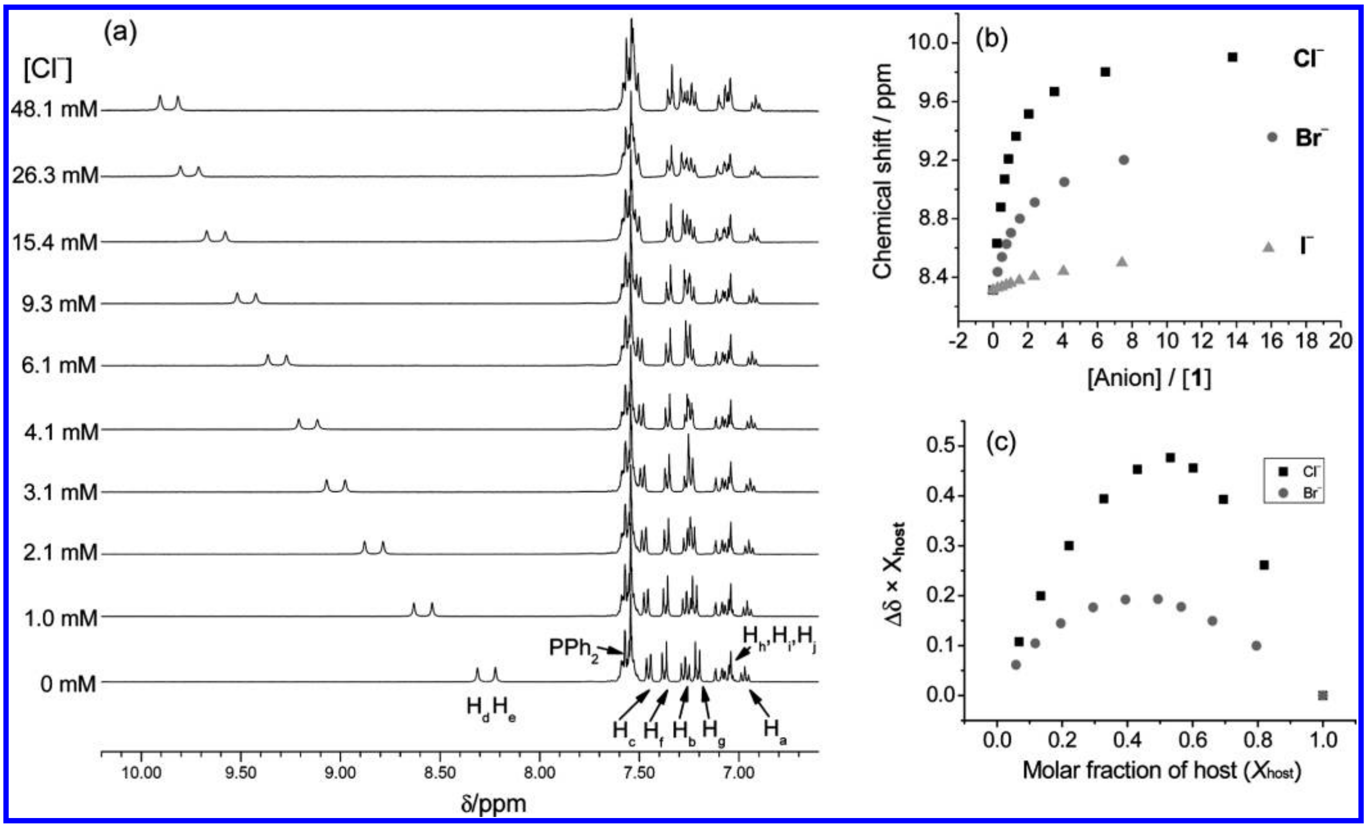


Figure 2. (a) ^{1}H NMR spectral changes of **1** (4.8 mM) upon addition of tetra-*n*-butylammonium chloride in CD_3CN-DMSO-d_6 (9:1, v/v). (b) ^{1}H NMR titration curves of **1** with the three different anions (Cl^-, Br^-, and I^-) in CD_3CN-DMSO-d_6 (9:1, v/v), where the changes of proton chemical shift of NH_d are monitored. (c) Job's plots for 1:1 binding of **1** with Cl^- and Br^-, showing a 1:1 stoichiometry. The changes of proton chemical shift of NH_d are monitored.

crown ether-containing luminophores.[30] In the solid state at 298 and 77 K, complex **1** is found to exhibit higher energy emission compared to that of **2**. The reason may be due to the fact that the crown ether unit with stronger electron-donating ability is expected to render the gold(I) atom in complex **1** more electron-rich and hence increases the thiolate-to-gold LMCT transition energy. The relatively large Stokes shift together with the observed luminescence lifetimes in the microsecond range are suggestive of a triplet parentage.

Ion-Binding Studies. The anion-binding properties of complex **1** have been quantitatively investigated by ^{1}H NMR spectroscopy. Figure 2a shows the ^{1}H NMR spectral changes of complex **1** upon the addition of Cl^- (as tetra-*n*-butylammonium salt) in CD_3CN-DMSO-d_6 (9:1, v/v). The tetra-*n*-butylammonium counterion with its large size is expected not to bind to the crown ether. Upon the addition of chloride, the signals of the two NH protons show a considerable downfield shift of up to 1.7 ppm, while the other proton signals are found to undergo essentially negligible changes, suggesting that the Cl^- ion would bind to the urea group of complex **1** through a hydrogen bonding interaction. Analogous investigations have also been carried out with larger halides such as Br^- and I^-, which show similar spectral changes in the ^{1}H NMR spectroscopy. However, the magnitude of the complexation-induced ^{1}H NMR shift is found to be smaller than that of Cl^- and is found to follow the trend $Cl^- > Br^- > I^-$ (Figure 2b), reflecting the decrease in charge density of the anionic guest species, since the ionic radii of Cl^-, Br^-, and I^- are 1.81, 1.95, and 2.16 Å, respectively.

A 1:1 binding mode has been proposed and confirmed by the method of continuous variation. Figure 2c shows the Job's plots for the binding of **1** with Cl^- and Br^- ions. A plot of the changes of proton chemical shift of NH_d versus X_1 (= [**1**]/([G] + [**1**])) shows a break point at a molar ratio of ca. 0.5, indicative of a 1:1 complexation stoichiometry. The binding constants K_s for **1** toward Cl^-, Br^-, and I^- are determined to be 599 ± 90, 109 ± 15, and 16 ± 2 M^{-1}, respectively, using the EQNMR program for a 1:1 binding model (Table 2).[31] The order of anion-binding affinity of complex **1** is found to be $Cl^- > Br^- \gg I^-$, consistent with the decrease in charge density of the anionic guest species. The experimental data are found to be in good agreement with the theoretical fits obtained from the EQNMR program using a 1:1 binding model.[31] The anion-binding properties of complex **1** with various halides (Cl^-, Br^-, and I^-) have also been studied using UV/vis and emission spectroscopy. However, insignificant spectral changes in the UV–vis absorption and emission spectra were observed.

Cation binding has also been studied using the ^{1}H NMR titration experiment. The addition of a Na^+ ion in the form of perchlorate salt to **1** leads to a slight downfield shift by ca. 0.1 ppm of the proton signals of the crown ether, as a result of the decrease in the electron

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[30] de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.

[31] Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

Table 2. Summary of Binding Constants of the Ditopic Receptor **1** for Halides in the Absence and in the Presence of 1 equiv of $NaClO_4$ in CD_3CN-d_6-DMSO (9:1, v/v) at 298 K[a]

halides[b]	Na^+ additive	binding constant (K_s/M^{-1})
Cl^-	none	599 ± 90
	Na^+	155 ± 20
Br^-	none	109 ± 15
	Na^+	c
I^-	none	16 ± 2
	Na^+	34 ± 5

[a] The binding constants were analyzed on the basis of the downfield shift of the urea NH signals. Errors in the binding constants were less than 15%. [b] Halides employed were as tetra-*n*-butylammonium salts. [c] Not determined.

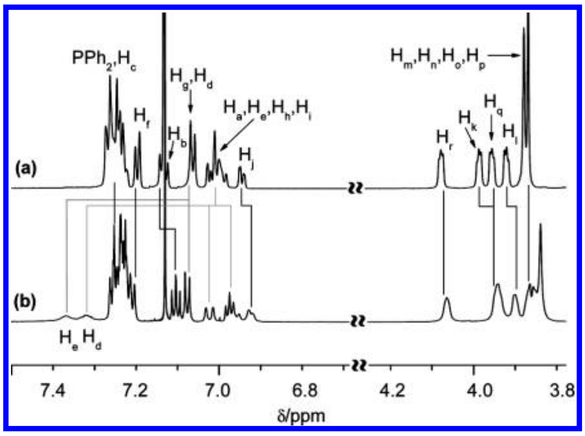

Figure 3. ^1H NMR spectra of **1** (5.6 mM) (a) in the unbound state and (b) as the [**1**·NaCl] adduct in $CDCl_3$.

density upon Na^+ binding to the crown cavity. These changes are also accompanied by a slight upfield shift of the urea NH protons by ca. 0.1 ppm, probably due to the binding of the Na^+ ion into the crown unit that destroys the intermolecular hydrogen bonding interaction between the NH of the urea unit and O atoms in the crown ether moiety. The binding event also shows a 1:1 stoichiometry by the method of continuous variation, and the binding constant K_s for Na^+ has been determined to be ca. 34 M^{-1}.

Experiments to study the cooperative effect of the presence of Na^+ on the halide binding have also been carried out by repeating the ^1H NMR titration experiments for anions in the presence of 1 equiv of $NaClO_4$. Different cooperativities have been observed for different halides. The addition of I^- to the $[\mathbf{1}\cdot Na]^+$ adduct gives a binding constant of 34 ± 5 M^{-1}, 2-fold larger than the binding constant for I^- with the free receptor **1**, indicating a positive cooperativity. For Cl^-, however, a negative cooperativity has been observed, and the binding constant in the presence of Na^+ is found to be smaller than that with free complex **1**. The above results agree with the trend that an anion with larger size tends to give the larger cation-induced affinity, which is consistent with the study reported by Smith and co-workers.[5]

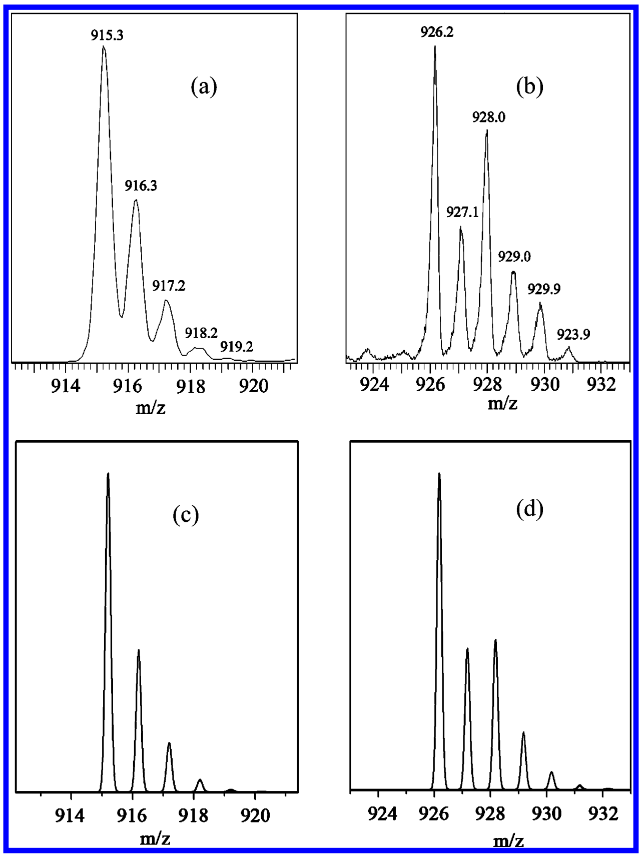

Figure 4. Expanded ion cluster of (a) $[\mathbf{1}\cdot Na]^+$ at *m*/*z* 915 from the positive ESI-mass spectrum and (b) $[\mathbf{1}\cdot Cl]^-$ at *m*/*z* 926 from the negative ESI-mass spectrum, in chloroform solution, and simulated isotopic patterns of (c) $[\mathbf{1}\cdot Na{-}1]^+$ and (d) $[\mathbf{1}\cdot Cl{-}1]^-$.

The binding property of the ditopic complex **1** has also been assessed by determining if the ditopic receptor **1** is capable of extracting solid salt, such as NaCl, into chloroform. Figure 3 shows the typical ^1H NMR spectral changes of complex **1** in $CDCl_3$ solution after stirring with an excess of solid NaCl for 20 h. The changes in the ^1H NMR chemical shifts of **1** suggest a rapid exchange process. Compared with the free complex, the proton resonances of the two urea NH signals of the [**1**·NaCl] adduct show a large downfield shift, suggesting the presence of hydrogen bonding interaction of the NH group with Cl^-. Meanwhile, the protons of the crown ether show a slight upfield shift, which is rather unusual and might be due to a ring current effect resulting from the π-stacking of the phenyl urea group with the benzocrown ether because of the ion pairing, which would bring the two binding units into close proximity. Complex **1** also shows good ability in the extraction of solid NaI, as revealed by the large downfield shift of the two urea NH signals. However, with KI and CsOTf, no obvious change in the ^1H NMR spectra can be observed, which may be due to the large cation size of K^+ and Cs^+ that cannot fit well into the cavity of the benzo-15-crown-5 unit. Although K^+ is well-known to be capable of binding to two benzo-15-crown-5 units in a sandwich binding mode,[21,22,32] the large steric bulk of the crown moiety ($-PPh_2B15C5$) in complex **1** might hinder the intermolecular sandwich binding with K^+. As a control, the crown-free analogue **2** has been investigated, which essentially shows negligible ^1H NMR spectral changes upon similar

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(32) (a) Xia, W. S.; Schmehl, R. H.; Li, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 5599. (b) Cacciapaglia, R.; Di Stefano, S.; Mandolini, L. *J. Am. Chem. Soc.* **2003**, *125*, 2224. (c) Yamauchi, A.; Hayashita, T.; Nishizawa, S.; Watanabe, M.; Teramae, N. *J. Am. Chem. Soc.* **1999**, *121*, 2319.

solid−liquid extraction, suggesting that the heteroditopic structure that could simultaneously bind the cation and anion is essential for salt transport.

The adduct of NaCl salt has also been confirmed by positive and negative ESI-MS experiments. After liquid−solid extraction, complex **1** exhibits intense signals at *m*/*z* 915 corresponding to the $[\mathbf{1} + \mathrm{Na}]^+$ adduct in the positive mode, and at *m*/*z* 928 corresponding to the $[\mathbf{1} + \mathrm{Cl}]^-$ in the negative mode (Figure 4). The close resemblance of the isotopic pattern of the two expanded ion clusters with the simulated patterns further supports the salt complexation. For the extraction of NaI salt, the signal at *m*/*z* 915 corresponding to the $[\mathbf{1} + \mathrm{Na}]^+$ could also be observed. However, the signal of the $[\mathbf{1} + \mathrm{I}]^-$ cannot be detectable, which may be due to the weak hydrogen bonding interaction between **1** and the I^- anion.

Conclusion

In summary, a novel ditopic receptor **1** based on a gold(I) phosphine thiolate complex has been successfully designed and synthesized, which contains a urea-functionalized thiolate as an anion-binding site, and a benzo-15-crown-5 ether unit in the phosphine auxiliary ligand for cation binding. In the solid state at 298 and 77 K, complex **1** is found to exhibit a slightly higher LMCT emission energy compared to that of **2**, which might be due to the presence of the stronger electron-donating crown ether moiety on the phosphine ligand of complex **1**, rendering the gold(I) atom more electron-rich, and hence increases the thiolate-to-gold LMCT transition energy. The anion-binding studies in the absence and in the presence of Na^+ have been carried out using ^{1}H NMR spectroscopy. The results show good 1:1 binding of **1** with anions, with a stability trend of $\mathrm{Cl}^- > \mathrm{Br}^- \gg \mathrm{I}^-$. In addition, for I^- with the largest size, the presence of Na^+ shows a positive cooperativity effect, giving a larger binding constant. The ditopic receptor **1** also shows a good ability to solubilize NaCl and NaI salts in organic chloroform solution, as evidenced by the ^{1}H NMR and ESI-MS experiments. Crown-free complex **2** shows essentially negligible capability in such solid−liquid transport of NaCl, suggesting the ditopic composition is essential for the complexation of simple salt.

It is envisaged that d^{10} gold(I) complexes, with rich photophysical properties and the two-coordinate nature, as well as the good affinity of gold with a variety of ligands, would provide an ideal platform to construct ditopic receptors. The design of various ditopic gold(I) complexes by incorporating different ligands with special receptor sites for recognition of guest molecules is in progress.

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