in the micellar system.[15] This is readily explained by assuming that the ABAP decomposes in the aqueous phase, as would be expected. More difficult to explain is the observation that ABAP decomposes 3 times less rapidly in 0.5 M SDS than in the liposome suspension, in water itself, in 0.1 M phosphate buffer (pH 7.0), or in 0.5 M sodium chloride/0.1 M phosphate buffer (pH 7.0).

Our present results show that *quantitative kinetic measurements on the autoxidation of heterogeneous systems are much less difficult than heretofore assumed.* It is interesting that in the liposomes, the charged, water-soluble initiator, ABAP, and inhibitor, TROLOX(−), though added after liposome formation, each appear to have had access to all layers of the multilamellar assembly. Our results also raise two intriguing possibilitites: first, that water soluble, chain-breaking antioxidants (either phenols or functionally related materials) may be present in vivo to supplement (lipid soluble) vitamin E; second, water soluble, chain-breaking antioxidants may have therapeutic value in the treatment of medical conditions (e.g., inflammation) suspected to involve lipid peroxidation.

(15) In water at 50 °C two azo initiators structurally related to ABAP have been reported to have *e* values of ca. 0.2, notably lower than their *e* values in organic solvents.[16]

(16) Pohlman, A.; Mill, T. *J. Org. Chem.* **1983**, *48*, 2133–2138.

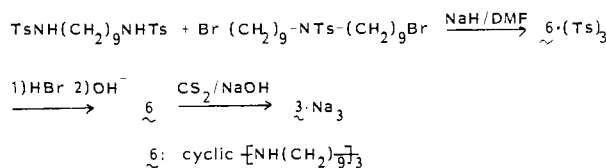## Macrocyclic Tridithiocarbamate as a Specific Uranophile

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Molecular design for host molecules specific to certain guests is one of the most important and valuable concepts developed recently.[1–4] However, host–guest binding is extremely sensitive to local environment depending on the interaction mode and well-known alkaline metal ion binding capacity of crown ethers, for example, is diminished in its magnitude remarkably in an aqueous solution. Apparently, design for host molecules showing strong binding toward certain metal ions in water requires considerably stronger host–guest coordination interaction than guest–water (or OH^-) interaction. This requirement is fulfilled when negatively charged macrocycles of appropriate sizes are prepared.[5,6] As a typical and illustrative example, we have made molecular design for hosts specific to uranyl, UO_2^{2+}, showing that appropriately designed "uranophiles" **1**[5] and **2**[6] bound UO_2 very strongly.

In addition to large association equilibrium constants, "uranophiles" must show large association rate constants to avoid such a competing side reaction as rapid formation of polynuclear complexes leading to precipitation of metal oxides.[7] Large rate

(1) Cram, D. J.; Cram, J. M. *Science (Washington, D.C)* **1974**, *183*, 803.

(2) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1.

(3) (a) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. (b) Breslow, R. *Science (Washington, D.C)* **1982**, *218*, 532. (c) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: New York, 1978.

(4) Tabushi, I.; Yamamura, K. *Top. Curr. Chem.* **1983**, *113*, 145.

(5) (a) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Tetrahedron Lett.* **1979**, 3515. (b) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Nature (London)* **1979**, *280*, 665.

(6) Tabushi, I.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E. *J. Am. Chem. Soc.* **1980**, *102*, 5947.

Scheme 1

constants are also important for practical applications (e.g., UO_2 extraction from sea current[8]).

Now we wish to report that the third macrocyclic polyanion, **3**, was newly prepared and it showed satisfactory properties, largest association constant of $10^{20.7}$, and strong characteristic absorption at 265 nm,[9] appropriate for direct analysis of rapid kinetic or precise equilibrium study. Preparation of **3** is rather straightforward as shown in Scheme I.[10] After silica gel chromatographic isolation, **6**(Ts)$_3$ was obtained in 29% yield: mp 103–105 °C; IR (KBr), 1330, 1160 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.2 and 7.6 (AB q, 12 H), 3.0 (t, 12 H), 2.4 (s, 9 H), 1.2–1.6 (m, 42 H). From the crude tosylate, **6** was obtained as a colorless solid in 82% yield by treatment with an alkaline solution followed by extraction: mp 53–54 °C; ^{1}H NMR δ 2.6 (t, 12 H), 1.3–1.7 (m, 45 H); mass spectrum, *m/e* 423 (M$^+$), 281, 142. Anal. Calcd for **6**·2H$_2$O: C, 71.05; H, 13.29; N, 9.15%. Found: C, 70.59; H, 13.30; N, 8.87. **3**·Na$_3$ was obtained as a colorless solid in quantitative yield (NMR determination): IR (neat) 960 cm^{-1}; 60-MHz ^{1}H NMR (D$_2$O, hexamethyldisilazane as an external standard) δ 4.1–4.5 (m, 12 H), 1.9–2.4 (m, 12 H), 1.6–1.9 (m, 30 H). 20-MHz ^{13}C NMR (D$_2$O, dioxane as an internal standard) δ 112.97 from dioxane (N^{13}CS$_2$), −12.01 (N^{13}C), −38.1 (NC^{13}C), −39.4 ∼ −41.2 (other ^{13}C).

The complex between UO_2^{2+} and **3** showed the characteristic absorption. The complex was very stable in the aqueous solution at high pH (7–12),[11] and formation of the UO_2^{2+}·**3** complex was conveniently followed by the characteristic absorption (using the absorption tail at 450 nm). By the spectroscopic determination of the concentration of UO_2^{2+}·**3**, equilibrium constants and rate constants were measured.[12] On the basis of these measurements, association constants were determined both for forward and backward substitution (eq 1) relative to reported association

$$UO_2(CO_3)_3 + 3 \underset{K}{\overset{K}{\rightleftharpoons}} UO_2 \cdot 3 + 3CO_3^{2-} \tag{1}$$
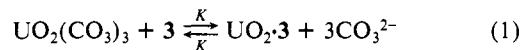
constant for carbonate.[13,14] Both relative constants independently determined are in a good agreement, affording a reliable association constant. This duplicate measurement is necessary for the too strong complexation, since some of dissociation steps easily becomes too slow to allow determination by titration procedure[15]

(7) (a) Ahrlen, D. S.; Hietanen, S.; Sillen, L. G. *Acta Chem. Scand.* **1954**, *8*, 1907. (b) Gustafson, R. L.; Richard, C.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 1526.

(8) Tabushi, I.; Kobuke, Y. *Bull. Soc. Sea Water Sci. Jpn.* **1982**, *36*, 205.

(9) λ$_{max}$ (ε) are for 3 260 and 283 nm (4.4 × 10^4 and 4.1 × 10^4 respectively) and for 3·UO$_2^{2+}$ complex 265 nm (3.8 × 10^4), free UO$_2^{2+}$ or UO$_2$(CO$_3$)$_3$ shows much smaller absorbance (free UO$_2^{2+}$, 265 nm (ε < 3.0 × 10^3) · UO$_2$(CO$_3$)$_3$ 265 nm (ε < 3.0 × 10^3).

(10) Similar preparation of macrocyclic amines in literature; (a) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268. (b) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Seesions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282.

(11) Hexacarboxylate–uranyl complex slowly precipitates at high pH; see ref 6. 3-Uranyl complex is stable after several days at pH 11.

(12) Detailed kinetic results will appear in a full-length article.

(13) Reported association constants between UO$_2^{2+}$ and carbonate are spread over a wide range: 10$^{23.0}$,[14a] 10$^{22.8}$,[14b] 10$^{21.5}$,[14a] 10$^{20.7}$,[14d] 10$^{18.3}$.[14e]

(14) Average value of the four independent and reliable association constants[14c,f,g,h] are chosen to give the value of 10$^{21.58±0.23}$. Association of UO$_2^{2+}$ with 3 was proven by us as a single step.[12] (a) Paramonova, V. I.; Nikolaeva, N. M. *Radiokhimiya* **1962**, *4*, 84. (b) Klygin, A. E.; Smirnova, Y. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 16. (c) Cinneide, S. O.; Scanlan, F. P.; Hynes, M. F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013. (d) Babko, A. K.; Kodenskaya, V. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1960**, *5*, 1241. (e) Bullwinkel, E. P. *USAEC* **1954**, RMO-2614. (f) Maya, L. *Inorg. Chem.* **1982**, *21*, 2895. (g) Isymbal, C. *Rapp. CEA-R-Fr., Commis. Energ. At.* **1969**, CEA-R-3476. (i) Lemire, R. J.; Tremaine, P. R. *J. Chem. Eng. Data* **1980**, *25*, 361.

(15) Tabushi, I.; Fujiyoshi, M. *Tetrahedron Lett.* **1978**, 2157.

on the basis of our preliminary kinetic results.

$$\vec{K}_{rel} = \frac{[UO_2 \cdot 3][CO_3^{2-}]^3}{[UO_2(CO_3)_3][3]} = 10^{-1.05}$$

$$\bar{K}_{rel} = \frac{[UO_2(CO_3)_3][3]}{[UO_2 \cdot 3][CO_3^{2-}]^3} = 10^{0.74}$$

$$K_{rel}(av) = \frac{[UO_2 \cdot 3][CO_3^{2-}]^3}{[UO_2(CO_3)_3][3]} = 10^{-0.89}$$

$$K = \frac{[UO_2 \cdot 3]}{[UO_2][3]} = 10^{20.7}$$

In conclusion, very appropriately designed[16] uranophile 3·Na₃ forms a stable complex with uranyl ion, which shows characteristic absorption in electronic spectrum, allowing precise equilibrium study. Association constant between uranyl and **3** in water is the largest among those directly measured.[17]

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(16) The diameter of the cavity is ca. 2.1 Å on the basis of the CPK model. Sulfur ligation is known as one of the strongest among those ever studied in the authors' laboratory.

(17) (a) Stronski, I.; Zielin, A.; Samotus, A.; Stasicka, Z.; Budesinsky, B. Z. *Anal. Chem.* **1966,** *222,* 14. Association constant of $10^{24.3}$ M⁻¹ was reported, based on indirect measurements. Our preliminary results show that the association constant is much smaller. (b) Budesinsky, B.; Hass, K.; Bezdekova, A. *Coll. Czech. Chem. Commun.* **1967,** *32,* 1528. Association constant of 10^{109} M⁻² was reported but molarity was not carefully determined.

Mixed-Metal Atom Cluster Compound Containing Silver(I) and Platinum(II)

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We wish to report the preparation and structural definition of a mixed-metal atom cluster compound that has a number of unusual features. It is the first example, so far as we know, of a compound that contains both silver–silver and silver–platinum bonds.

By reaction of equimolar quantities of AgNO₃ and (NBu₄)₂ [*trans*-PtCl₂(C₆F₅)₂][1] in methanol according to eq 1, a yellow solid

$$2(NBu_4)_2[t\text{-}PtCl_2(C_6F_5)_2] + 2AgNO_3 \rightarrow$$
$$2(NBu_4)NO_3 + (NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4] \quad (1)$$

compound, **1**, is precipitated. This compound was first characterized by elemental analysis, conductance, and infrared spectroscopy.[2] At room temperature the solid darkens to pale brown within about 1 month whereas an acetone solution decomposes in a few hours even at −25 °C, depositing AgCl. The other products of decomposition have not yet been identified. This instability made it very difficult to obtain crystals but by slow diffusion of *i*-C₃H₇OH into an acetone solution at −25 °C this was accomplished, and the structure was then solved by X-ray crystallography.[3]

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(1) Uson, R.; Forniés, J.; Martinez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980,** 888.

(2) Calcd for C₅₆H₇₂N₂F₂₀Cl₄Ag₂Pt₂: C, 35.38; H, 3.79; N, 1.47. Found: C, 35.20; H, 3.73; N, 1.48. Λ (~5 × 10⁻⁴ M in acetone): 218 ohm⁻¹ cm² mol⁻¹; IR 770 cm⁻¹ (ν_{C-F}), 320 cm⁻¹ (broad, ν_{Pt-Cl}).
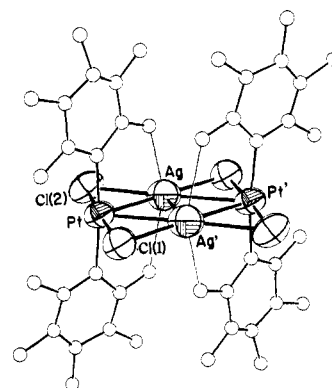

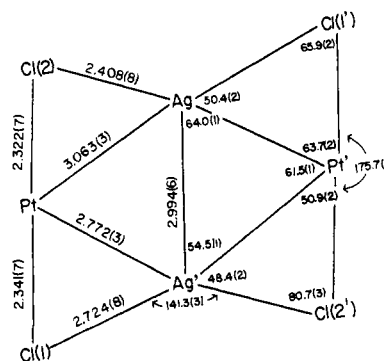**Figure 1.** ORTEP drawing of the entire [Pt₂Ag₂Cl₄(C₆F₅)₄]²⁻ ion.

Figure 2. Drawing of the central Ag₂Pt₂Cl₄ plane, showing principal bond lengths and angles.

The entire molecular structure is shown in Figure 1 and the central, essentially planar Ag₂Pt₂Cl₄ unit, with principal bond lengths and angles, is shown in Figure 2. The molecule is rigorously centrosymmetric. Considering first the central Ag₂Pt₂Cl₄ unit, we note that the metal atoms would conventionally be assigned oxidation numbers of I and II for Ag and Pt, respectively, and that each Pt atom is linked to an essentially trans-planar set of Cl and C atoms with normal bond lengths: Pt–Cl, 2.322 (7), 2.341 (7) Å; Pt–C, 2.04 (3), 2.07 (3) Å. The two PtCl₂(C₆F₅)₂ units then embrace a central Ag₂ unit in which the Ag–Ag distance is 2.994 (6) Å. Each silver atom then has close contact with one platinum atom, 2.772 (3) Å, which surely represents a Pt–Ag bond of considerable strength as well as a longer contact, 3.063 (3) Å, with the other platinum atom. The strength of Pt–Ag bonding across this longer distance is a moot point. Each Ag atom also has contacts to Cl atoms at distances of 2.408 (8) Å, which represents a strong bonding interaction, and 2.724 (8) Å, which probably indicates some fractional bonding. The Ag–Ag distance is near the high end of the range (vide infra) that is spanned by previous cases in which Ag–Ag bonding has been presumed to occur.

One of the most remarkable features of this structure is the close approach of two ortho fluorine atoms to each Ag atom, at distances of 2.60 (1) and 2.69 (1) Å. The expected length[4] of an Ag–F bond would be 1.98 Å, so that the interaction here does not approach true bond formation, but it would appear that it must contribute to the stability of the cluster, since, otherwise, rotation about the Pt–C bonds could easily lead to an apparent overall lessening of nominally nonbonding contacts.

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(3) Crystal system: triclinic (*P*$\bar{1}$ assumed), with *a* = 12.438 (9) Å, *b* 13.160 (7) Å, *c* = 11.129 (8) Å, *α* = 103.53 (5)°, *β* = 101.27 (6)°, *γ* = 74.75 (5)°, *Z* = 1. Of 2621 measured reflections, those 1616 unique reflections with $F^2 \geq 3\sigma(F^2)$ were corrected for Lorentz and polarization effects, absorption and anisotropic decay of 45% over 157 h of exposure, and used to solve the structure. Final refinement of 293 variables for 43 atoms (24 refined anisotropically) led to $R = 0.079$ and $R_w = 0.097$. A list of atomic positional parameters is available as supplementary material.

(4) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 403.