Metallamacrocycles

Synthesis of a Metallophilic Metallamacrocycle: A Hg^{II}···Cu^{I}···Hg^{II}···Hg^{II}···Cu^{I}···Hg^{II} Interaction**

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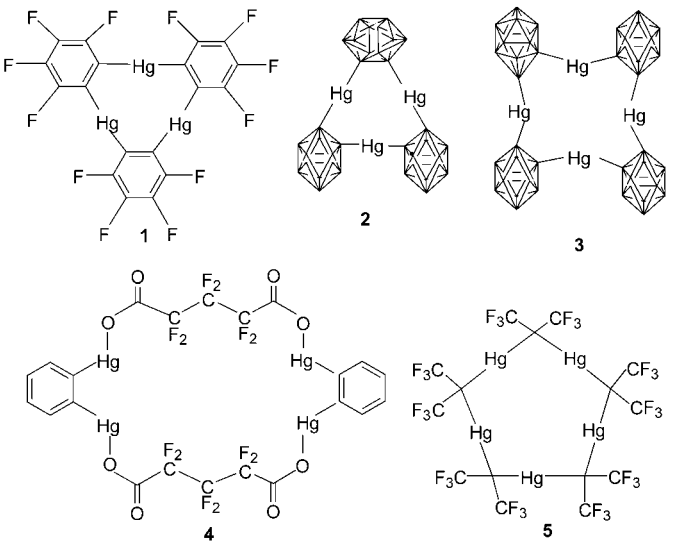
Macrocyclic multidentate Lewis acids have attracted considerable interest as electrophilic hosts in supramolecular chemistry. The electrophilic hosts generally use tin,[1] silicon,[2] boron,[3] germanium,[4] and mercury[5–8] atoms as binding sites for neutral and anionic electron-rich guests. Polydentate organomercurials are the most investigated series of all the multidentate Lewis acids and have applications as catalysts[9] and sensors.[10] These organomercurials include trimeric perfluoro-*o*-phenylenemercury (**1**),[6a] [9]mercuraborand-3 (**2**), [12]mercuracarborand-4 (**3**),[7] the 24-membered macrocyclic perfluoroglutarate **4**,[8b] and the cyclic pentameric $[(CF_3)_2CHg]_5$ macrocycle **5**.[6b] Some of these compounds exhibit short intermolecular Hg···Hg metallophilic interactions in the solid state, and these metallophilic interactions are often associated with unusual luminescent properties.[5b,c,11]

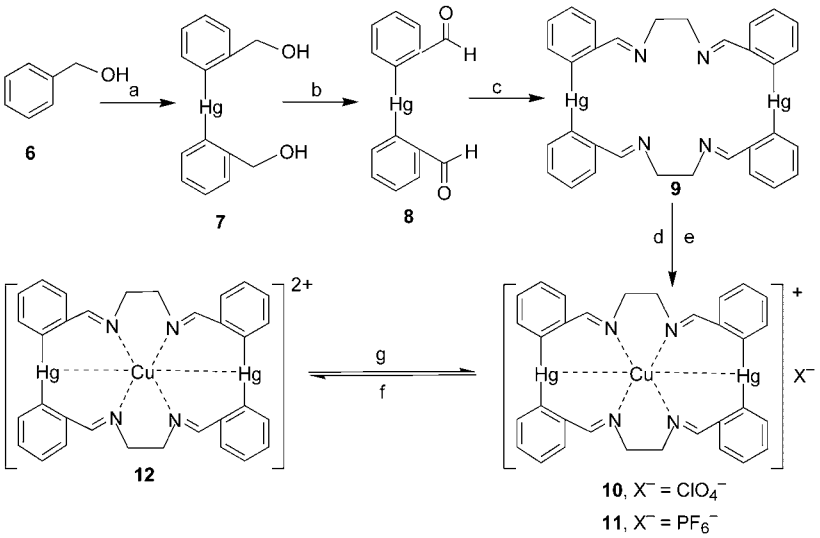
Whereas the interaction of metallamacrocycles with electron-rich species has been studied extensively, their coordination through short metal–metal interactions with cations is still largely unexplored. However, the work of Catalano et al. on mixed-metal metallocryptands[12] formed by self-assembly is a notable exception. Severin and co-workers also reported a similar metallamacrocycle, an organometallic [12]metallacrown-3 species, that was obtained by self-assembly.[13]

Herein, we present a metallamacrocycle that contains both a Lewis acidic mercury center and basic nitrogen atoms in a preorganised macrocycle and a cation complex of a mercuramacrocycle that exhibits metallophilic interactions between the coordinated Cu^{I} and Hg^{II} centers.

The white and air-stable, novel 22-membered metallamacrocycle **9** was prepared by [2+2] cycloaddition of **8**[14] with ethylenediamine in high yield without recourse to a template. The precursor **8** was synthesized from benzyl alcohol by lithitation.



Ortho-lithiation of benzyl alcohol, followed by treatment with mercuric chloride, afforded compound **7**, which was oxidized with pyridinium chlorochromate (PCC) to give **8** in good yield (Scheme 1). The Hg···O intramolecular interaction



Scheme 1. Synthetic route to the 22-membered mercuramacrocycle **9** and its Cu^{I} complexes: a) *n*BuLi (2 equiv), −78 °C, THF, $HgCl_2$; b) PCC, CH_2Cl_2; c) $H_2NCH_2CH_2NH_2$, MeOH; d) $[Cu(CH_3CN)_4]ClO_4$, MeOH; e) $Cu(CH_3COO)_2$, NH_4PF_6, MeOH; f) coulometry; g) left to stand.

in **8** presumably plays a role in macrocyclization. To synthesize the Cu^{I} complex, ligand **9** was treated with one equivalent of $[Cu(CH_3CN)_4]ClO_4$ in methanol to afford an orange–yellow-colored complex **10**. In an attempt to prepare a Cu^{II} complex, **9** was treated with $Cu(OCOCH_3)_2$, followed by an excess of ammonium hexafluorophosphate. An orange–yellow-colored Cu^{I} complex **11** was produced unexpectedly with PF_6^- as the counter ion (Scheme 1). Both complexes were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopic analysis, as well as MS(ESI) and elemental analysis. The reduction of the Cu^{II} ion without a reducing agent is not

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[**] This work was supported by DST and DRDO. We are grateful to Prof. G. K. Lahiri for providing access to coulometric equipment.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

 DOI: 10.1002/ange.200462487

unprecedented. Lai and co-workers[15] observed a similar reduction of a Cu^{II} ion when treated with a quinquedentate macrocycle, and they suggested that the autoreduction occurred because of the electron-donating properties of the ligand or the geometry of the complex formed.

Single crystals of **10** were isolated as orange needles from a solution in acetonitrile/ether for X-ray diffraction studies.[16] The structure confirms the novel coordination of the Cu^{I} center to all four nitrogen atoms and to the two mercury atoms to give a distorted octahedral geometry (Figure 1). The

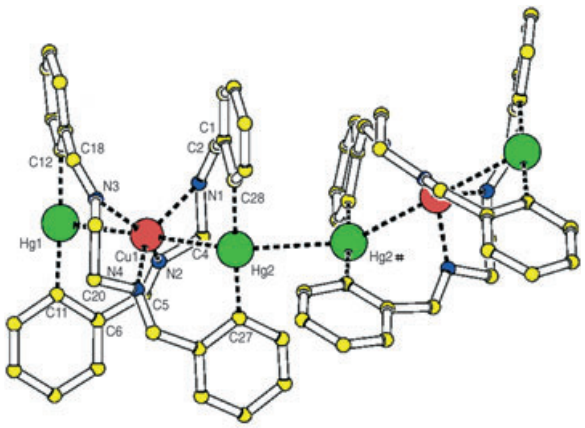

Figure 1. PLATON view of compound **10** that shows the dimerization of compound **10** through a Hg···Hg intermolecular homometallic d^{10}···d^{10} interaction and Hg···Cu d^{10}···d^{10} heterometallic interactions. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–Hg1 2.921(7), Cu1–Hg2 2.919(7), Hg2–Hg2# 3.203(4), Hg1-Cu1-Hg2 177.88(3), Cu1-Hg2-Hg2# 154.40(17), C11-Hg1-C12 177.80(18), C27-Hg2-C28 177.21(18), Hg2-Cu1-N1 69.70(12), Hg2-Cu1-N4 71.03(10), Cu1-Hg2-Hg2# 154.40(17).

Cu···Hg interatomic distances (Cu1–Hg1 2.921 Å and Cu1–Hg2 2.919 Å) are shorter than the sum of the van der Waals radii of the copper and mercury atoms ($r_{vwd} = 1.40$ and 1.75 Å, respectively).[17] However, this Cu···Hg distance is longer than the Cu···Hg distance found in the polymetallic mesocycle $[Hg\{Fe[Si(OMe)_3](CO)_3(\mu\text{-dppm})\}_2Cu]^+$.[18] Further inspection of the crystal packing revealed that two cations of **10** are linked by a Hg···Hg intermolecular interaction of 3.20 Å to give a chain of six d^{10} ions. The Hg···Hg distance is longer than the Hg···Hg distance in metallic mercury (3 Å)[19] but much shorter than those observed in other structures with Hg···Hg interactions[5b,c,d,g,20] and the calculated value for the perpendicular $HgMe_2$ dimer (3.50 Å).[17b] However, this distance in **10** is slightly longer than that observed for bis(trimethylsilyl)mercury.[21] The important feature of this molecule is the presence of two types of d^{10}···d^{10} metallophilic interaction: a homometallic Hg^{II}···Hg^{II} interaction and a heterometallic Hg^{II}···Cu^{I} interaction.

Complexes **10** and **11** show a well-defined reversible redox wave with $E_{1/2}$ values of 0.55 and 0.57 V versus the saturated calomel electrode (SCE) and ΔE values of 0.078 and 0.080 V with I_{pc}/I_{pa} values of 1.06 and 1.03, respectively. The green-colored solution of the Cu^{II} complex **12** could be generated by coulometric oxidation of the orange-colored solution of **10** in acetonitrile at 0.725 V in a cyclic-voltammetry cell. The Cu^{II} complex could be stabilized for a short time by quenching the solution at 77 K. The ESR spectrum of **12** shows $g_{II(av)}$ at 2.54 with $A_{(av)} = 190$ G and $g_{\perp(av)}$ at 2.09 with $A_{\perp(av)} = 67.50$ G. The green-colored Cu^{II} complex is reduced again to the orange-colored Cu^{I} complex within half an hour when left to stand in solution.

The electronic absorption spectrum of **9** in acetonitrile solution exhibits a strong absorption band at 292 nm ($\varepsilon = 6400\,M^{-1}cm^{-1}$). Complex **10** shows a low-energy band at 410 nm ($\varepsilon = 800\,M^{-1}cm^{-1}$) and a strong peak at 292 nm in the same solvent. The band at 410 nm is attributed to a metal-to-ligand charge transfer. Cu^{I} complexes **10** and **11** were found to be luminescent at room temperature and also at 77 K both in acetonitrile solution and in the solid state. The acetonitrile solution of **10** shows a very weak emission at $\lambda_{max} = 445$ nm. Upon cooling to 77 K and in the solid state, the emission spectrum becomes more intense. Upon excitation at $\lambda_{max} = 450$ nm in the solid state, the emission spectra exhibited a sharp band at $\lambda_{max} = 485$ nm, along with weaker bands at 530 and 545 nm. Detailed photophysical studies are in progress.

Successful trapping of a Cu^{I} ion in a mercuramacrocycle demonstrates that a metallamacrocycle can be used to entrap suitably sized metal ions with metal–metal interactions in a preorganized system. This approach can be extended to prepare various mixed-metal systems, in particular those with d^{10}···d^{10} interactions, with interesting structural and luminescent properties.

Received: November 1, 2004
Published online: February 3, 2005

Keywords: copper · heterometallic complexes · mercury · metallacycles · metal–metal interactions

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[16] Crystal structure data for **10**: $C_{32}H_{28}ClHg_2N_4O_4$, $M_w = 1032.75$. Monoclinic, space group $I2/a$ with $a = 18.6441(10)$, $b = 10.3912(8)$, $c = 31.9312(18)$ Å, $\alpha = 90°$, $\beta = 95.741(7)°$, $\gamma = 90°$, $V = 6155.1(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.229$ mg m^{-3}, $2.64 < \theta < 26.73°$, crystal dimensions $0.24 \times 0.16 \times 0.08$ mm, $\mu = 10.768$ mm^{-1}, $T = 293(2)$ K. A total of 46961 reflections were measured in the range $2.64 < \theta < 26.73°$ ($-23 < h < 23$, $-13 < k < 13$, $-40 < l < 40$) with 6500 unique reflections ($R_{int} = 0.1056$). Full-matrix least-squares refinement on F^2 $R1 = 0.0229$, ($I > 2\sigma(I)$) $R1 = 0.0577$ (all data); $wR2 = 0.0311$ ($I > 2\sigma(I)$), $wR2 = 0.0355$. Further details are given in the Supporting Information. CCDC 253481 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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