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Notes

Hexanuclear Mercury−Silver Complexes. Novel Coordination for Bridging Mesityl and Triflate Groups

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Introduction

Mercury forms heterometallic complexes with transition metals and has been recognized as “universal glue”[1,2] in the systematic synthesis of clusters. A great variety of gold−mercury intermetallic compounds are known;[3] however, it is noteworthy that only a few clusters with mercury-11 group metals have been reported, some related to gold[4−10] and only recently with silver[11] $[AgHg_2(\mu\text{-dppm})_3]^{3+}$.

Continuing with our latest research in heterometallic mesityl-bridging compounds by addition of different metal fragments to gold mesityl complexes,[12−14] in this work we select $[Hg(mes)_2]$[15] as starting material and report on the polynuclear compounds $[HgAg_2(mes)_2A_2]_2$ (A= SO_3CF_3 (**1**), ClO_4 (**2**)). The hexanuclear complex **1** displays two interesting features: a novel coordination for two mesityl groups and two triflate anions acting as tridentate ligands to four silver atoms (Figure 1). So far, we are unaware of reports on the latter coordination modes.

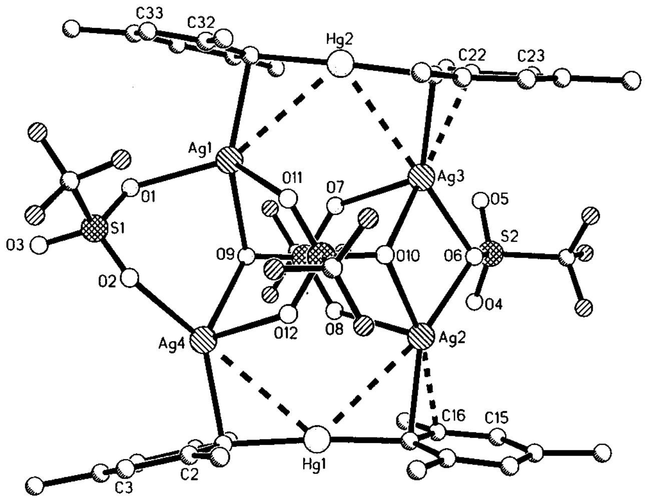

Figure 1. Crystal structure of complex **1**. Radii are arbitrary. H atoms and the CH_2Cl_2 molecule are omitted for clarity.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer over the range 4000−200 cm^{-1} (Nujolmulls between polyethylene sheets). The NMR spectra were recorded on a Varian UNITY 300 spectrometer {^{1}H (300 MHz) and ^{19}F (282.2 MHz)} using tetramethylsilane and $CFCl_3$ as references. The C, H, and S analyses were performed with a Perkin Elmer 2400 microanalyzer. Conductivities were measured in acetone with a Philips PW 9509 apparatus. Mass spectra, LSIMS, were recorded on a VG Autospec with a Cs gun and 3-nitrobenzyl alcohol as matrix.

Materials. $[Hg(mes)_2]$[15] was obtained according to the literature procedures. ^{1}H-NMR ($CDCl_3$, 295 K): δ 7.00 (s, 2H, *m*-H, [$^5J_{^{199}Hg-H}$ = 28.0 Hz]), 2.50 (s, 6H, *o*-Me, ($^3J_{^{199}Hg-H}$ = 11.2 Hz]), 2.28 (s, 3H, *p*-Me). All others reagents are commercially available.

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of Compounds. $[HgAg_2(mes)_2A_2]_2$ (A = SO_3CF_3 (1), ClO_4 (2)). To a stirred solution of $AgClO_4$ (41.5 mg, 0.2 mmol) or $AgSO_3CF_3$ (51.4 mg, 0.2 mmol) in 10 mL of diethyl ether was added $[Hg(mes)_2]$ (43.9 mg, 0.1 mmol) dissolved in 20 mL of dichoromethane. The mixture reaction was allowed to react for 1 h. The solvent was removed by vacuum distillation to 5 mL, and addition of 20 mL of *n*-hexane gave **1** and **2** as white crystals which were filtered of and dried *in vacuo*. (**1**) Yield: 65%. ^{1}H-NMR ($CDCl_3$, 295 K): δ 6.99 (s, 2H, *m*-H, [$^5J_{^{199}Hg-H}$ = 14.5 Hz]), 2.48 (s, 6H, *o*-Me), 2.29 (s, 3H, *p*-Me). ^{19}F-NMR ($CDCl_3$, 295 K): δ −77.3 (s). Anal. Calcd for $C_{40}H_{44}Ag_4F_{12}Hg_2O_{12}S_4$: C, 25.2; H, 2.3; S, 6.7. Found: C, 25.5; H, 2.4; S, 6.35. **(2)** Yield: 72%. ^{1}H-NMR ($CDCl_3$, 295 K): δ 6.90 [s, 2H, *m*-H, ($^5J_{^{199}Hg-H}$ = 29.9 Hz)], 2.46 [s, 6H, *o*-Me], 2.35 [s, 3H, *p*-Me]. Anal. Calcd for $C_{36}H_{44}Ag_4Cl_4Hg_2O_{16}$: C, 25.3; H, 2.6. Found: C, 25.0; H, 2.7.

X-ray Structure Determination. The crystal (a colorless tablet *ca.* 0.34 × 0.19 × 0.19 mm) was mounted in inert oil (type RS 3000, Riedel de Haën) on a glass fiber. Data were collected using monochromated Mo Ka radiation (λ = 0.710 73). A Stoe-Siemens four-

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Table 1. Details of Data Collection and Structure Refinement for the Complex **1**·CH_2Cl_2

chemical formula	$C_{41}H_{46}Ag_4Cl_2F_{12}Hg_2O_{12}S_4$	fw	1990.58
a	11.540(2) Å	space group	$P\bar{1}$
b	12.299(3) Å	T	−100 °C
c	20.885(5) Å	λ	0.710 73 Å
α	102.78(2)°	ρ_{calcd}	2.342 Mg m^{-3}
β	101.380(10)°	μ(Mo Kα)	7.116 mm^{-1}
γ	92.38(2)°	R^a (F, $F > 4\sigma(F)$)	0.0418
V	2822.7(11) $Å^3$	wR^b (F^2, all reflns)	0.0877
Z	2		

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ag(1)−O(1)	2.346(8)	Ag(1)−C(31)	2.368(10)
Ag(1)−O(9)	2.485(8)	Ag(1)−O(11)	2.532(7)
Ag(1)−Hg(2)	3.2797(14)	Ag(2)−O(6)	2.335(8)
Ag(2)−C(11)	2.346(10)	Ag(2)−O(10)	2.504(8)
Ag(2)−O(8)	2.557(8)	Ag(2)−C(16)	2.599(12)
Ag(2)−Hg(1)	3.2689(14)	Ag(3)−C(21)	2.284(10)
Ag(3)−O(6)	2.327(8)	Ag(3)−O(10)	2.457(8)
Ag(3)−O(7)	2.479(7)	Ag(3)−C(22)	2.658(11)
Ag(3)−Hg(2)	3.1012(11)	Ag(4)−O(2)	2.297(8)
Ag(4)−C(1)	2.363(10)	Ag(4)−O(9)	2.468(7)
Ag(4)−O(12)	2.528(8)	Ag(4)−Hg(1)	3.3863(12)
Hg(1)−C(11)	2.093(11)	Hg(1)−C(1)	2.114(10)
Hg(2)−C(31)	2.096(11)	Hg(2)−C(21)	2.112(11)

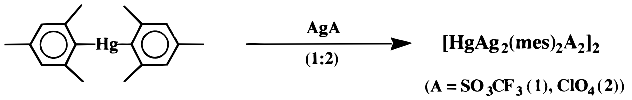
O(1)−Ag(1)−C(31)	115.9(3)	O(1)−Ag(1)−O(9)	82.1(3)
C(31)−Ag(1)−O(9)	144.1(3)	O(1)−Ag(1)−O(11)	119.6(3)
C(31)−Ag(1)−O(11)	105.9(3)	O(9)−Ag(1)−O(11)	88.6(2)
O(6)−Ag(2)−C(11)	144.2(3)	O(6)−Ag(2)−O(10)	81.5(3)
C(11)−Ag(2)−O(10)	133.2(3)	O(6)−Ag(2)−O(8)	92.4(3)
C(11)−Ag(2)−O(8)	97.0(3)	O(10)−Ag(2)−O(8)	87.3(3)
O(6)−Ag(2)−C(16)	113.9(3)	C(11)−Ag(2)−C(16)	31.8(3)
O(10)−Ag(2)−C(16)	164.7(3)	O(8)−Ag(2)−C(16)	91.5(3)
C(11)−Hg(1)−C(1)	175.8(4)	C(31)−Hg(2)−C(21)	177.8(4)

circle diffractometer with a Siemens low-temperature attachment was used. Cell constants were refined from the settings of 52 reflections in the range $2\theta = 25-32°$. An absorption correction based on ψ scans was applied with transmission factors 0.708−0.991. The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93.[16] H atoms were included with a riding model, with methyl protons rigid. Further details are given in Table 1, and selected bond lengths and angles in Table 2.

Results and Discussion

We have recently[12−14] reported that the reaction of mesityl gold complexes, e.g. [Au(mes)(PPh_3)] or [Au(mes)($AsPh_3$)], with silver or gold electrophilic derivatives, such as [Ag(OSO_2CF_3)], [Ag($OClO_3$)], [Ag(A)(PPh_3)] (A= OSO_2CF_3, $OClO_3$), or [Au($OClO_3$)(PPh_3)], is a useful way to synthesize heteronuclear mesityl bridge complexes. In a similar way, the mercury(II) derivative [Hg$(mes)_2$] reacts with [Ag(OSO_2CF_3)] or [Ag($OClO_3$)] in a 1:2 molar ratio in dichloromethane to give solutions from which white air- and moisture-stable complexes, **1** and **2**, respectively, can be isolated in ∼70% yield (Scheme 1). A similar reaction with other silver complexes, such as [Ag(A)(PPh_3)] (A = OSO_2CF_3, $OClO_3$), gives the heteronuclear complexes **1** and **2** as the main products. The same reaction with gold complexes, [Au($OClO_3$)(PPh_3)] or [Au$(tht)_2$]ClO_4 (tht = tetrahydrothiophene), gives decomposition to metallic gold.

Scheme 1



Complexes **1** and **2** behave as nonconductors in dichloromethane solutions. In addition to the usual absorptions observed for mesityl, their IR spectra show bands between 1378 and 1180 cm^{-1} (**1**) and at 1119 (vs, br), 1022 (vs, br), and 623 (s, br) (**2**) assigned to covalent triflate[17a] and perchlorate,[17b] respectively. The ^1H-NMR spectra at room temperature exhibit three resonances, *m*-H, *o*-Me, and *p*-Me, whereas at low temperature (−65 °C) a broad singlet for the methyl protons (*o*- and *p*-) can be seen. The $^{19}F\{^1H\}$-NMR spectrum of **1** shows one resonance at −77.3 ppm assigned to covalent triflate[18] which splits into two resonances (1:1 ratio) at −74.4 and −78.7 ppm at −60 °C. The mass spectra (LSIMS+) are very informative, showing signals that may be assigned to the parent ion with loss of one triflate (**1**) or perchlorate (**2**) group, $[M - A]^+$ at *m/z* 1757 (7%) (**1**) and 1608 (9%) (**2**). This highlights the hexanuclearity of these clusters and their stability. Other fragments are present in the mass spectra of these clusters such as $[M - Ag - 2A]^+$ at *m/z* 1499 (39%) (**1**) and 1400 (78%) (**2**) or $[^1/_2M - A]^+$, at *m/z* 803 (100%) (**1**) and 755 (97%) (**2**). It is worth noting that the mass spectra of both compounds also show peaks assigned to $[Hg_2Ag(mes)_4]^+$ at *m/z* 985.

Crystals of **1** suitable for X-ray diffraction studies were obtained from dichloromethane−diethyl ether. Compound **1** exists as a hexanuclear [Hg_2Ag_4] complex which can be described as two [$HgAg_2(mes)_2$] moieties linked by four triflate anions via coordination to the silver atoms. Each trinuclear moiety has two mesityl ligands acting as bridges between a mercury and a silver atom through C_{ipso}. In each moiety, a bridging mesityl group displays an additional interaction between one of the C_{ortho} and one silver center. The mesityl groups are approximately in parallel planes as observed in [$HgPh_2$][19] and, consequently, not symmetrically oriented with respect to the Hg−Ag axis. However, the four mesityl ring planes are nearly perpendicular to the plane through the atoms Hg−Ag−C_{ipso}, as in other complexes with bridging mesityl ligands.[12,13,20,21] The bridging mesityl groups [between Hg(2) and Ag(3) and between Hg(1) and Ag(2)] exhibit the greatest deviation from 90° [83.9(2)° and 82.4(3)°], probably as a consequence of the weak C_{ortho}−Ag interaction [C(22)−Ag(3) 2.658(11) Å and C(16)−Ag(2) 2.599(12) Å]. However, there are no significant differences in the C−C ring distances of the four mesityl groups, showing that the extra interaction should be very weak. The mercury atoms are two-coordinate with C−Hg−C angles of 175.8(4)° [C(1)−Hg(1)−C(11)] and 177.8(4)° [C(31)−Hg(2)−C(21)], and the bond distances Hg-C [2.093(11)−2.114(10) Å] are quite close to that found in [$HgPh_2$][19] [2.085(7) Å]. The four Ag−C_{ipso} distances range from 2.284(10) to 2.368(10) Å and are slightly longer than in $[\{Ag(mes)\}_4]$[20] [average length 2.20(3) Å]. They are very close to those reported for $[\{AuAg(mes)(PPh_3)(tht)\}_2](SO_3CF_3)_2$[12]

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[2.326(3) Å] and $[\{Au(mes)(AsPh_3)\}_2Ag](ClO_4)$[13] [2.27(2) Å]. The nonbonded Hg−Ag distances lie in the range 3.101(1)−3.386(1) Å.

On the basis of the bond lengths presented above, we propose that, rather than a 3c−2e bond, the aromatic C_{ipso} atom is σ-bonded to the mercury center but π-bonded to the silver by an interaction of the electron-rich π orbital of C_{ipso}, perpendicular to the plane of the aryl ring, with an empty orbital of the silver center. This coordination mode has also been reported for some copper aryl complexes.[22,23] The silver centers Ag(3) and Ag(2) require more electron density from the C_{ortho} than Ag(1) and Ag(4), but the similarity in the C−C phenyl ring distances suggests that this interaction is relatively weak. To the best of our knowledge, this is a new form of coordination for a mesityl bridging ligand.

The two $[HgAg_2(mes)_2]$ moieties are connected by four triflate anions which hold together at least one silver center of each unit. There are three different types of coordination: (a) monodentate bridging through one oxygen ($\mu_2 2{:}3\kappa^2$O), (b) bidentate through two oxygen ($\mu_2 1\kappa$O,4κO′), and (c) tridentate connecting four silver centers and two central triflates [($\mu_4 1\kappa$O,4κO′,$2{:}3\kappa^2$O″) and ($\mu_4 2\kappa$O,3κO′,$1{:}4\kappa^2$O″)]. The Ag−O distances are longer in the tridentate coordination, (average in (c) is 2.502(8) Å) than in the other types (averages in (a) and (b) are 2.332(8) and 2.324(8) Å, respectively). Although some examples of mono- and bidentate coordination of the triflate anion have been reported,[16,18,24] this is the first example of a triflate anion bonded to four metallic centers.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for complex **1** is available on the Internet only. Access information is given on any current masthead page.

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