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Inorganic−Organic Hybrid Lamella of Di- and Tetranuclear Silver−Carbene Complexes

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Summary: Di- and tetranuclear silver−carbene complexes of inorganic−organic hybrid lamella were isolated and structurally characterized. The dinuclear complex has an inorganic Ag_2Br_2 core in the center and four long alkyl chains stretched outward, while the tetranuclear complex has an $Ag-Ag_2Br_4-Ag$ core and eight alkyl chains.

The use of imidazol-2-ylidenes (a type of N-heterocyclic carbene) as ligands in transition-metal complexes has recently received growing interest, because this type of carbene has electronic properties comparable to those of phosphines and forms stable complexes with many metal ions.[1] The unique properties possessed by these metal−carbene complexes allow their application in many catalytic reactions,[2] supramolecules, and materials.[3]

N-Heterocyclic carbene complexes of silver, prepared by the complexation of free carbene to silver, were first reported in 1993.[4] Recently, we reported an alternative method to prepare Ag−bimy (bimy = N,N-disubstituted benzimidazol-2-ylidene) complexes by treatment of benzimidazolium salts with Ag_2O.[5] These complexes further act as effective carbene transfer agents for the synthesis of palladium− and gold−bimy carbene complexes.[3b,5] These mild reaction conditions have been employed successfully by others.[6] As part of our continuing goal to search for metal-containing liquid crystals and inorganic−organic hybrid lamella, liquid crystalline imidazolium salts were treated with Ag_2O in an attempt to synthesize long-chain liquid crystalline silver−carbene complexes. To our surprise, lamellar dinuclear and tetranuclear silver−carbene complexes of identical percent compositions were observed and isolated. The results with long lipophilic side chains appear to be different from the experience we have on the silver−carbene complexes with short side chains. We have noted that the presence of two isomeric Ag−carbene complexes has been proposed and reported,[6a] although the exact nature was not certain. In this work, we report preliminary structural results. These complexes can serve as models of inorganic−organic hybrid lamella. The hydrophobic chain encapsulated silver ions are potentially useful as antimicrobial agents and in the chemistry of metal containing liquid crystals.

Reaction of $[(C_{14}H_{29})_2\text{-im}]Br\cdot H_2O$ (im = N,N-disubstituted imidazolium ion) with Ag_2O in CH_2Cl_2 for ~1 h followed by removal of the solvent produces a white powdery solid. Recrystallization of the crude product from acetone gives rodlike crystals which were structurally analyzed as the dinuclear silver−mono(carbene) complex $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$ (imy = N,N-disubstituted imidazol-2-ylidene).[7] On the other hand, recrystallization from CH_2Cl_2/hexane gives platelike crystals which were analyzed as the tetranuclear silver−bis(carbene) complex $[Ag((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$.[8] The dinuclear Ag_2 species can be obtained from the tetra-

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[7] $[(C_{14}H_{29})_2\text{-im}]Br\cdot H_2O$ (0.200 g, 0.36 mmol) and Ag_2O (0.042 g, 0.18 mmol) were added to CH_2Cl_2 (30 mL). The solution was stirred at room temperature for 1 h. The resultant solution was filtered, and the filtrate was dried under vacuum. The white residue was then recrystallized from CH_2Cl_2/hexane to yield a pale yellow crystalline product (0.221 g, 95%). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation from the above solution. ^1H NMR ($CDCl_3$, 25 °C): δ 6.96 (s, 4H, CH), 4.07 (t, $^3J = 7$ Hz, 8H, CH_2), 1.80 (m, 8H, CH_2), 1.27−1.40 (m, 88H, CH_2), 0.88 (t, $^3J = 7$ Hz, 12H, CH_3). Anal. Calcd for $C_{62}H_{120}N_4Ag_2Br_2$: C, 57.41; H, 9.32; N, 4.32 Found: C, 57.72; H, 9.48; N, 4.36. Crystal structure analysis of $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$: $C_{62}H_{120}N_4Ag_2Br_2$, $M_r = 648.59$, monoclinic, space group $P2_1/c$, $a = 22.254(2)$ Å, $b = 16.5519(14)$ Å, $c = 9.2187(8)$ Å, $\alpha = 90°$, $\beta = 98.314(2)°$, $\gamma = 90°$, $V = 3360.0(5)$ Å^3, $Z = 2$, $F(000) = 1368$, $D_c = 1.282$ g cm^{-3}, $T = 296$ K, crystal dimensions 0.2 × 0.2 × 0.2 mm; intensity data collected on a Bruker P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å), 5606 nonzero (2σ) reflections out of 21 622 collected with $2 < 2\theta < 50°$. The structure solution was accomplished with the aid of Bruker SHELXTL, and refinement was conducted using Bruker SHELXTL. R1 = 0.0521, wR2 = 0.0810, C, N, Ag, and Br atoms are anisotropic, and H atoms are isotropic. The final Fourier difference map showed a residual electron density of 0.687 e Å^{-3}.

[8] When the crude product obtained from ref 7 was recrystallized from acetone, platelike crystals were obtained. ^1H NMR ($CDCl_3$, 25 °C): δ 6.96 (s, 8H, CH), 4.07 (t, $^3J = 7$ Hz, 16H, CH_2), 1.80 (m, 16H, CH_2), 1.27−1.40 (m, 176H, CH_2), 0.88 (t, $^3J = 7$ Hz, 12H, CH_3). Anal. Calcd for $C_{124}H_{240}N_8Ag_4Br_4$: C, 57.41; H, 9.32; N, 4.32. Found: C, 57.48; H, 9.39; N, 4.26. Crystal data for $[Ag((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$: $C_{124}H_{240}Ag_4Br_4N_8$, $M_r = 2594.36$, triclinic, space group $P\bar{1}$, $a = 9.507(3)$ Å, $b = 11.420(2)$ Å, $c = 33.520(9)$ Å, $\alpha = 83.02(3)°$, $\beta = 82.081(17)°$, $\gamma = 87.56(3)°$, $V = 3576.5(15)$ Å^3, $Z = 2$, $F(000) = 2736$, $D_c = 2.409$ mg m^{-3}, $T = 296$ K, crystal dimensions 0.15 × 0.10 × 0.10 mm; 11 085 nonzero (2σ) reflections out of 9146 collected with $3.5 < 2\theta < 45°$. The structure solution was accomplished with the aid of Bruker SHELXTL, and refinement was conducted using Bruker SHELXTL. R1 = 0.0835, wR2 = 0.1294, C, N, Ag, and Br atoms are anisotropic, and H atoms are isotropic. The final Fourier difference map showed residual electron density of 0.395 e Å^{-3}.

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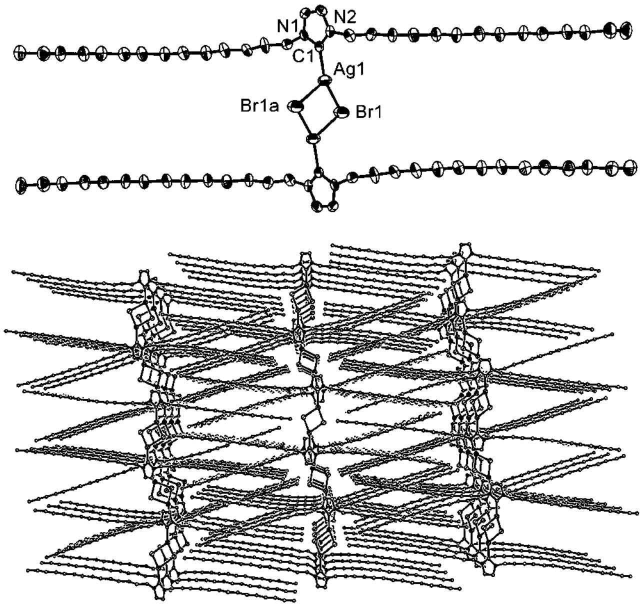

Figure 1. (a, top) ORTEP drawing of $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$ (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ag(1)−C(1), 2.094(5); Ag(1)−Br(1), 2.4980(7); Ag(1)−Br(1a), 2.9248(8); C(1)−N(1), 1.343(5); C(1)−N(2), 1.349(5); Br(1)−Ag(1)−Br(1a), 95.18(2); C(1)−Ag(1)−Br(1), 153.06(12); C(1)−Ag(1)−Br(1a), 111.59(12); N(1)−C(1)−N(2), 104.6(4); N(1)−C(1)−Ag(1), 125.9(4); N(2)−C(1)−Ag(1), 129.5(4). (b, bottom) Crystal packing of $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$.

nuclear Ag_4 species and vice versa. Possibly, the slight difference in solubility allows the isolation of the Ag_2 and Ag_4 species. In $CDCl_3$, the two species give identical ^1H and ^{13}C NMR spectra. In addition, no ^{13}C−Ag coupling has been observed. These results suggest the occurrence of a fast exchange between the two species in solution. Crystal structures of these species are given in Figures 1 and 2, with important bond distances and bond angles in the figure captions.

The structure of $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$ (Figure 1a) can be considered as a pair of mono(carbene) $[Ag((C_{14}H_{29})_2\text{-imy})Br]$ associates through intermolecular Ag···Br interactions. The molecular structure of the dinuclear complex reveals a distorted H-shaped geometry, having an Ag_2Br_2 ring plane in the center and four alkyl chains, with two up and two down, being extended "perpendicular" to the Ag_2Br_2 core plane to form a rod. In the central core, each of the two imy planes coordinates to a silver atom and twists ~87.4° from the Ag_2Br_2 plane in an opposite direction, The central Ag_2Br_2 ring has one normal Ag−Br bond distance of 2.4980(7) Å and a slightly long Ag−Br distance of 2.9248(8) Å. Stacking of the molecules (Figure 1b) gives alternating layers of Ag_2Br_2 cores and interdigitated alkyl chains.

The structure of the tetranuclear complex (Figure 2a) can be considered as an $[Ag_2Br_4]^{2-}$ anion intercalated between two $[Ag(carbene)_2]^+$ cations with weak Ag(cation)···Ag(anion) interactions (~3.0 Å). It thus has an Ag_4 core sitting in the center and eight alkyl chains stretched outward. The cation $[Ag((C_{14}H_{29})_2\text{-imy})_2]^+$ has a conformation similar to that of the cation of the liquid crystalline $[Au((C_{16}H_{33})_2\text{-bimy})_2]Br$;[9] both can be described as a distorted four-legged table. In the $[Ag_2Br_4]^{2-}$ anion, each silver ion bonds to three bromides with Ag−Br distances of 2.531(2), 2.6573(16), and 2.682(2) Å and Br−Ag−Br angles of 127.30(7), 129.30(6), and 99.91(6)°. The average bond distance is longer, while the average bond angle is smaller, than reported[10] for $Ag_2Br_4^{2-}$. This is consistent with the weak Ag···Ag interactions observed in this Ag_4 compound. Although crystal packing (Figure 2b) of this tetrasilver complex also exhibits a layer structure consisting of inorganic Ag_4 cores and long alkyl chains, the tail-to-tail stacking of alkyl chains is noninterdigitated. We have noted that the Ag−carbene transfer technique[5] has been applied to the synthesis of short-side-chain Au−carbene complexes but not the long-side-chain complexes. The liquid crystalline Au−bimy compounds of long side chains were reported to have been synthesized by treating benzimidazolium salts with $Au(SMe_2)Cl$ under basic phase transfer conditions.[9] In this work, in an attempt to synthesize long-side-chain Au−carbene compounds by the Ag−carbene transfer technique, a heterotetranuclear (Au_2Ag_2) compound was identified. Again, this result differs from those with short side chains. A preliminary X-ray

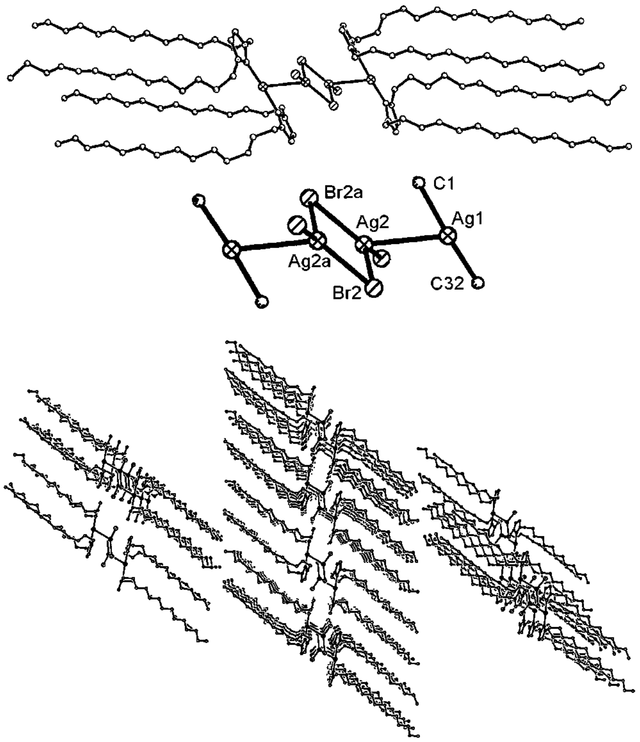

Figure 2. (a, top). ORTEP drawing of $[Ag((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$ (50% thermal ellipsoids), with an enlarged and labeled drawing of the central core. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(2), 3.0068(18); Ag(1)−C(1), 2.094(5); Ag(1)−C(32), 2.138(13); Ag(2)−Br(2), 2.681(2); Ag(2)−Br(2a), 2.6582(17); C(1)−Ag(1)−C(32), 174.6(7); C(1)−Ag(1)−Ag(2), 111.1(4); C(32)−Ag(1)−Ag(2), 70.7(4); Br(1)−Ag(2)−Br(2a), 127.30(7); Br(1)−Ag(2)−Br(2), 129.32(6); Br(2a)−Ag(2)−Br(2), 99.90(6); Br(1)−Ag(2)−Ag(1), 86.96(6); Br(2a)1−Ag(2)−Ag(1), 125.65(6); Br(2)−Ag(2)−Ag(1), 77.81(5); Ag(2a)−Br(2)−Ag(2), 80.10(6). (b, bottom) Crystal packing of $[Ag((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$.

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diffraction study shows that the heterotetranuclear Au−bis(carbene) complex $[Au((C_{14}H_{29})_2\text{-imy})_2]_2[Ag_2Br_4]$[11] exhibits an Au−$Ag_2Br_4$−Au inorganic core with short Au···Ag interactions (∼3.0 Å). The structure can also be considered as analogous to the Ag_4 species, with an $[Ag_2Br_4]^{2-}$ anion intercalated between two $[Au(carbene)_2]^+$ cations.

In this work, two stoichiometrically identical Ag−carbene complexes, dinuclear silver−mono(carbene) and tetranuclear silver−bis(carbene) complexes, were isolated and structurally characterized. The dinuclear compound consists of an inorganic Ag_2Br_2 core and an organic layer of interdigitated alkyl chains. The tetranuclear compound consists of an inorganic Ag−Ag_2Br_4−Ag core and an organic layer of noninterdigitated alkyl chains. Using the Ag−carbene transfer technique, a heterotetranuclear Au_2Ag_2 compound, having a structure similar to that of the Ag_4 species, was identified. It is interesting to note that while crystals of the Ag_2 species are rod-shaped, crystals of the Ag_4 species are thin plates with an area as large as 0.5 × 0.5 cm^2. The different chain-packing patterns of the rodlike molecules may result in the difference of crystal growth. Although these silver−carbene complexes are nonmesogenic, a preliminary observation shows that a mixture (1:1) of the silver−carbene complex and its corresponding imidazolium salt displays liquid crystal properties. While encapsulation of silver ions by hydrophobic layers can effect their diffusion through a biomembrane, the liquid crystalline behavior of these Ag−carbene compounds in the imidazolium salt may further enhance the diffusion process and thus may be effective as alternative antimicrobial agents in the treatment of burn wounds. Work is underway to assess this possibility.

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Supporting Information Available: Tables of crystal data, positional parameters for non-hydrogen and hydrogen atoms, bond distances and angles, and anisotropic thermal parameters for the compounds $[Ag((C_{14}H_{29})_2\text{-imy})Br]_2$, $[Ag((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$, and $[Au((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Ag_2O (20.6 mg, 0.089 mmol) was added to a CH_2Cl_2 solution (30 mL) of $[(C_{14}H_{29})_2\text{-im}]Br\cdot H_2O$ (100.0 mg, 178 mmol). The suspension became clear after stirring for 2 h at room temperature. $Au(SMe_2)Cl$ (26.3 mg, 89 mmol) then was added, and the resultant solution was stirred for an additional 2 h. The final solution was dried under vacuum. The white solid was recrystallized from acetone/CH_2Cl_2 to produce a colorless platelike crystalline product in 70% yield. ^1H NMR (ppm, $CDCl_3$): δ 7.58 (s, 8H, CH), 4.29 (t, $^3J = 7$ Hz, 16H, CH_2), 1.88 (m, 16H, CH_2), 1.18−1.31 (m, 176H, CH_2), 0.87 (t, $^3J = 7$ Hz, 24H, CH_3). Anal. Calcd for $C_{124}H_{240}N_8Au_2Ag_2Br_4$: C, 53.92; H, 8.72; N, 4.04. Found: C, 55.04; H, 8.83; N, 4.17. The slight discrepancy in the C analysis between the calculated and observed values is due to the presence of a trace of $[Au((C_{14}H_{29})_2\text{-im})_2]Br$. Crystal structure analysis: $[Au((C_{14}H_{29})_2\text{-imy})_2]_2[AgBr_2]_2$, $M_r = 509.24$, triclinic, space group $P\bar{1}$, $a = 9.543(7)$ Å, $b = 11.224(3)$ Å, $c = 33.901(13)$ Å, $\alpha = 84.17(2)°$, $\beta = 82.28(6)°$, $\gamma = 88.06(3)°$, $V = 3579(3)$ Å^3, $Z = 1$, $F(000) = 1432$, $D_c = 1.286$ g cm^{-3}, $T = 296$ K, crystal dimensions 0.5 × 0.5 × 0.1 mm; intensity data were collected on a Bruker P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å), 11 430 nonzero (2σ) reflections out of 13 605 collected with $2 < 2\theta < 50°$. The structure solution was accomplished with the aid of Bruker SHELXTL, and refinement was conducted using Bruker SHELXTL. R1 = 0.1234, wR2 = 0.2721. N, Ag, Br, and parts of C atoms are anisotropic, and H atoms are isotropic. The final Fourier difference map showed residual electron density of 2.802 e Å^{-3}. There is no doubt as to the structure of the molecule; however, owing to disorder in the alkyl chains, the *R* factor is rather large. This does not interfere with a reasonable determination of the Au−Ag_2Br_2−Au core. See the molecular structure and tables of X-ray data and distances and angles in the Supporting Information.