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Unusual Manifestation of Closed-Shell Interactions in Silver(I) Complexes: Crystal Structure of Catena-bis(4-aminobenzoato)disilver(I) Acetone Solvate with Ligand Unsupported Chains of Repeated Rhombohedral Ag$_4$ Units

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Despite the repulsion expected between two closed-shell metal cations, there are numerous examples of Ag(I) coordination compounds with short Ag−Ag contacts that have been structurally characterized, ranging from dimers to intricate high-nuclearity clusters. In a vast majority of these compounds, the Ag−Ag interactions are assisted by the presence of bridging or capping ligands. Whether the short Ag−Ag distances, comparable to the Ag−Ag separation in metallic silver [2.889 Å], are the result of d^{10}−d^{10} attractive metal−metal interactions, or if the silver ion geometries are maintained by the bridging or capping ligand architectures is a central question in the chemistry of these complexes. This issue has been a matter of some debate due to the scarcity of unambiguous experimental evidence of silver aggregates that are stable in the absence of stabilizing ligands.[1−3] Only a few examples of ligand unsupported Ag(I) aggregates have been reported, such as dimeric structures[4−6] and polymeric chains.[7,8] In this communication, we present a ligand unsupported silver(I) aggregate with a higher complexity and shorter Ag−Ag distances than hitherto reported, namely catena(μ_3-*O,O′,N*-4-aminobenzoato) (μ_2-*O,N*-4-aminobenzoato)disilver(I) acetone solvate.

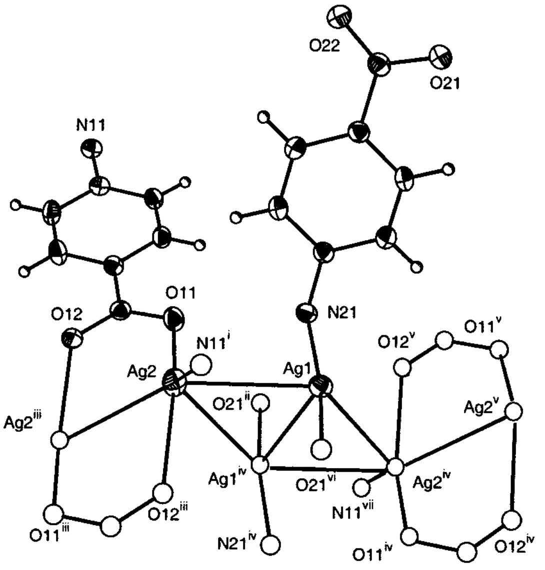

Figure 1. The asymmetric unit with displacement ellipsoids at the 50% probability level for non-hydrogen atoms. Symmetry generated atoms are shown with open circles. Selected bond lengths [Å]: Ag1−O21$^{\mathrm{vi}}$ 2.135(2), Ag1−N21 2.144(2), Ag2−N11$^{\mathrm{i}}$ 2.341(3), Ag2−O11 2.188(2), Ag2−O12$^{\mathrm{iii}}$ 2.322(2).[12]

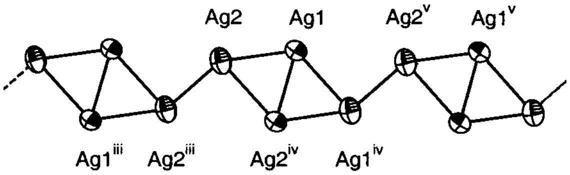

Figure 2. Geometry of the Ag(I) chains. The Ag2−Ag2$^{\mathrm{iii}}$ and Ag2$^{\mathrm{iv}}$−Ag2$^{\mathrm{v}}$ interactions are supported by bis(*O,O′*-carboxylate) bridges, other Ag−Ag interactions are ligand unsupported. The displacement ellipsoids are drawn at the 75% probability level. Selected bond lengths [Å] and angles [deg]: Ag1−Ag1$^{\mathrm{iv}}$ 2.9870(5), Ag1−Ag2 3.0252(4), Ag1−Ag2$^{\mathrm{iv}}$ 3.2974(4), Ag2−Ag2$^{\mathrm{iii}}$ 2.9460(6), Ag1−Ag1$^{\mathrm{iv}}$−Ag2 66.52(1), Ag1−Ag1$^{\mathrm{iv}}$−Ag2$^{\mathrm{iv}}$ 57.30(1), Ag2−Ag1−Ag2$^{\mathrm{iv}}$ 123.81(1), Ag2−Ag2$^{\mathrm{iii}}$−Ag1 145.62(2), Ag2−Ag2$^{\mathrm{iii}}$−Ag1$^{\mathrm{iv}}$ 90.17(1), Ag1−Ag2−Ag1$^{\mathrm{iv}}$ 56.19(9).[12]

The title compound was obtained by heating 1:1 stoichiometric quantities of silver(I) nitrate and potassium *p*-aminobenzoate in water/acetone (80/20), yielding pale yellow crystals that are relatively stable, both chemically and photochemically.[9] The crystals are assembled by rhombohedral Ag$_4$ units that coordinate eight *p*-aminobenzoate ligands, four through the carboxylic oxygen and four through the amino nitrogen atoms (Figure 1).[10] The rhombohedral units are not stabilized by bridging or capping ligands but solely linked by Ag−Ag interactions (Figure 2). The Ag$_4$ units are further linked to form infinite chains by Ag−Ag interactions supported by bis carboxylato-*O,O′*) bridges [*d*(Ag−Ag) = 2.9460(6) Å]. The carboxylato group exhibits a slightly unsymmetrical syn−syn bridging mode. The Ag−O distances of 2.135(2) and 2.341(3), with an O−Ag−O angle of 123.3(3)°, are comparable to those found in the dimeric structures of several known silver(I) carboxylates.[11] The Ag$_4$ units are strictly planar, where successive units are off-set by 0.387(2) Å, giving an angle of 3.3° between the Ag$_4$ plane and the plane defined by all Ag atoms in the chain. Ag1 is linearly coordinated, neglecting Ag−Ag interactions, by one oxygen from a monodentately coordinating carboxylate group and one amine nitrogen atom [Ag−O

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[9] Synthetic, analytical, and spectroscopical data have been deposited as Supporting Information.

[10] Crystallographic data was obtained using a Bruker SMART CCD diffractometer at 298 K. Monoclinic, space group $P2_1/n$, a= 7.3875(5), b = 15.352(1), c = 15.0632(1) Å, β = 103.080(1)°, V = 1664.2(2) Å^3, Z = 4, R$_1$ = 0.0310 and wR$_2$ = 0.0861.

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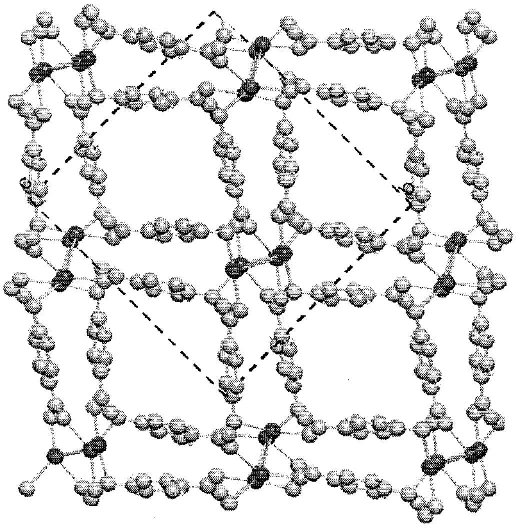

Figure 3. View of the extended lattice down the *a* axis, parallel to the Ag(I) chains, showing continuous channels with an opening size of ∼ 3.6 × 3.9 Å. The channels are occupied by acetone molecules, which are omitted for clarity.

2.135(2), Ag−N 2.144(2) Å, and O−Ag−N 168.83(9)°]. Ag2 coordinates two bidentately bridging carboxylate groups and one amino nitrogen atom in a distorted trigonal geometry, again neglecting the Ag−Ag interactions.

The eight bidentate *p*-aminobenzoate ligands originating from each Ag_4 unit link four adjacent chains. The shortest interplanar distance between the ligand aromatic rings is 3.680(3) Å, a distance that suggests that aromatic $\pi-\pi$ may have an appreciable importance for the nonbonded crystal organization.[13] Adjacent Ag(I) chains are tilted 57.8° with respect to each other. The crystal arrangement results in continuous channels parallel to the *a* axis and to the silver(I) chains, with an opening size of ∼ 3.6 × 3.9 Å (Figure 3). The solvent accessible volume is 308.3 Å, which is 18.5% of the total unit cell volume.[14] The acetone molecules are highly disordered, as expected from this loosely constraining environment.

A relatively stable intermediate polymorph can be isolated in the synthesis of the title compound,[6] namely catena(μ_4-*O,O,O′,N*-4-aminobenzoato) (μ_3-*O,O′,N*-4-aminobenzoato) disilver(I), and the structure has been determined.[15] Detailed comparison is unfortunately hindered by the limited accuracy of this structure determination ($R = 0.098$), mainly due to decomposition of the crystal. The intermediate structure consists of linear tetramers, which corresponds to Ag1−Ag2−Ag2^{iii}−Ag1^{iii} in Figure 1, with the central bond assisted by a bis-carboxylate bridge [*d*(Ag−Ag)=2.92(4) Å] and the terminal bonds with one carboxylate bridge [*d*(Ag−Ag)=3.16(4) Å]. The central carboxylate ligands are tridentate and bridge a second tetramer, corresponding to Ag1^{v}−Ag2^{v}−Ag2^{iv}−Ag1^{iv}, which is further linked to the first tetramer by a carboxylate bridge between Ag1 and Ag2^{iv} [*d*(Ag−Ag)= 3.60(4) Å]. This arrangement results in continuous chains analogous to those found in this study. The transformation proceeds through a change of the terminal bridging carboxylate ligands to a monodentate mode accompanied by a shortening of the Ag−Ag distance to 2.9870(2) Å. Work is currently in progress at this laboratory on detailed analyses of this and related transformations.

The Ag1−Ag1^{iv} (2.9870(5) Å) and Ag1−Ag2 (3.0252(4) Å) distances observed in the title compound are significantly shorter than those found in the limited number of structures containing ligand unsupported Ag−Ag interactions that have been reported in the literature. With the 2,4′-bipyridine ligand, helical chains are observed where adjacent chains are unambiguously linked by ligand-unsupported dimeric metal−metal interactions [*d*(Ag−Ag) = 3.1526(6) Å].[4] Polymeric chains interlinked by unsupported dimeric Ag−Ag interactions [*d*(Ag−Ag) = 3.161(4) Å] are also observed in silver imidazolate[5] and in unsupported dimeric contacts [*d*(Ag−Ag) = 3.227(2) Å] between pyrazolate-bridged trimers.[6] With a betaine derivative, conventional bis(carboxylato-*O,O′*) bridged dimers are extended into a stairlike chain, where silver ions in adjacent chains have a comparatively short distances [*d*(Ag−Ag] = 3.269(2), 3.346(2) Å].[7] Unsupported Ag−Ag contacts are also observed in M[(Ag(CN)$_2$] salts, usually consisting of stacked layers of Ag(CN$_2$)$^-$ alternating with layers of the cation in a variety of two-dimensional topologies. The Ag−Ag distances are generally longer than 3.5 Å, but for Tl[Ag(CN)$_2$] a short Ag−Ag distance of 3.110(3) Å is reported.[8]

The attractive interactions between gold(I) metal ions have been emphasized in several studies, and the term aurophilic interaction has been used. Theoretical calculations indicate the attraction as a correlation effect strengthened by relativistic effects.[16] Silver−silver interactions have received considerably less attention, presumably due to the scarcity of unambiguous experimental evidence of such interactions, for example, silver aggregates that are stable in the absence of stabilizing bridging or capping ligands. Recently, however, several articles have appeared that treat these interactions at different levels of theory. Ab initio calculations on ligand-supported dimeric structures conclude that electron correlation energies capture most of the physics of the Ag(I)−Ag(I) interaction.[3] The theoretically predicted geometries were in close agreement with the experimentally observed geometries. For larger systems, ab initio or density functional methods require prohibitively long computation times, and methods using frozen core approximations must be used.[2] Interestingly, the geometry of the cluster of Ag(I) ions in the title compound show a remarkable similarity with the planar trapezoidal form calculated as the stable form for neutral Ag_5 clusters.[17] This geometry is also experimentally observed as the stable pentamer in mass-selected silver cluster ions from a sputtered jet, which were neutralized and matrix isolated in solid argon, according to the results of Raman measurements.[18]

To conclude, the direct evidence for ligand unsupported tetranuclear Ag(I) interactions have been presented. Work is currently in progress in this laboratory with an investigation of the physical properties of this and related compounds.

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Supporting Information Available: Text describing synthetic procedures and analytical and spectroscopical data, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Symmetry codes: *i*: x-0.5, 0.5-y, z-0.5; *ii*: 0.5 + *x*, 0.5 − *y*, 0.5 + z; *iii*: 2 − *x*, −*y*, 2 − *z*; *iv*: 1 − *x*, −*y*, 2 − *z*; *v*: 1 − *x*, *y*, *z*.; *vi*: 0.5 − *x*, y − 0.5, 1.5 − *z*; *vii*: 1.5 − *x*, *y* − 0.5, 2.5 − *z*.

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