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Factors Involved in the Nuclearity of Silver Thiosemicarbazone Clusters: Cocrystallization of Two Different Sized Tetranuclear Silver(I) Clusters Derived from a Phosphinothiosemicarbazone Ligand

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The reaction of silver acetate with a phosphinothiosemicarbazone ligand, HLPPh, yielded the tetranuclear silver compound $[Ag_4(LPPh)_4] \cdot 2MeOH$ (**1**), which after recrystallization results in the cocrystallization of two different silver clusters, $[Ag_4(LPPh)_4]^a$-$[Ag_4(LPPh)_4]^b \cdot 8MeOH$ (**2**). The factors involved in the assembly of tetranuclear compounds derived from thiosemicarbazone ligands and the structural differences between the two clusters are analyzed herein. Additionally, HLPPh and complex **1** exhibit photoluminescence in solution at room temperature.

Coordination chemistry of thiosemicarbazone ligands has attracted considerable attention in the last 50 years.[1] The variety of structures displayed by the metal complexes, but mainly their pharmacological properties, makes these compounds of special interest.[2]

By contrast, the structural chemistry of silver complexes with thiosemicarbazone ligands remains still quite unexplored to date, probably because of the instability and the formation of highly insoluble polymeric species. Although the first silver(I) stoichiometry with these types of ligands was reported in the early 1980s,[3] we had to wait until 2004 for the first hexameric $Ag_6S_6N_6$ complex derived from a salicylaldehyde thiosemicarbazone to be published.[4] Later on, a new route to obtaining $Ag_4S_4N_4$ cluster helicates using a pentadentate thiosemicarbazone ligand was reported.[5] Our group contributed in 2006 with a hexanuclear silver(I) cluster $Ag_6S_6N_6$, derived from a thione−triazole ligand formed after a cyclization process.[6] A more recent report has described a tetranuclear $Ag_4S_4N_4$ cluster derived from 4*N*-morpholyl-2-acetylpyridine thiosemicarbazone.[7] The formation of hexanuclear silver(I) clusters versus tetranuclear ones, using bidentate [NS] or tridentate [XNS] thiosemicarbazones (X = O, N), can be possible by exclusively using the sulfur and the imine nitrogen atoms from six thiosemicarbazone units, with the X donor atom remaining unbound, if it exists.[4] However, in other cases, tetranuclear $Ag_4X_4N_4S_4$ aggregations are formed by coordination of four thiosemicarbazone strands, involving the additional X donor atom from the carbonylic precursor.[4,7] Both cases, tetranuclear and hexanuclear, do have in common the participation of the thiosemicarbazone ligands in a deprotonated mode.

In parallel, it is well-known that one of the most convenient strategies to assembling M(I) cluster compounds (M = Cu, Ag, Au) uses aromatic phosphines as ligands or coligands.[8] While the aurophilicity principle has been extensively used to describe the strong closed-shell metal−metal interactions of gold clusters,[9] surprisingly few examples of argentophilic behavior have been reported,[10] probably because of the weaker metallophilic nature of silver compared to gold.

With these considerations in mind and with the aim to gaining a better insight into the coordinative factors involved in the assembly of silver clusters using thiosemicarbazones, we decided to use a phosphinothiosemicarbazone ligand. These types of ligands were previously employed to stabilize

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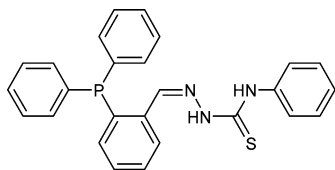(10) Jansen, M. *Angew. Chem., Int. Ed.* **1987**, *99*, 1136–1149.

Figure 1. Ligand HLPPh.

platinum(II) and gold(III) monomer species.[11] Our objective was to determine if the introduction of a phosphorus atom, and therefore the use of a [PNS] tridentate phosphinothiosemicarbazone, would exert any influence in the nuclearity of the assembled silver compound. The ligand, 2-[2-(diphenylphosphino)benzylidene]-*N*-phenylthiosemicarbazone (HLPPh; Figure 1) will potentially act as a [PNS] tridentante.[12] The reaction of HLPPh with silver(I) acetate in methanol afforded a powdery solid, tentatively identified as [Ag$_4$(LPPh)$_4$]·2MeOH (**1**).[12] Slow evaporation from the mother liquors yielded the crystalline compound [Ag$_4$(LPPh)$_4$]^a[Ag$_4$(LPPh)$_4$]^b·8MeOH (**2**).[13]

Remarkably, the complex contains two different cocrystallized tetranuclear silver(I) clusters in the asymmetric unit, additionally solvated by eight methanol molecules. Separate representations of the two different tetramers, labeled as a and b, are shown in Figure 2. Central cores of both clusters a and b are represented in Figure 3a,b, including representative bond lengths.

The X-ray data analysis reveals that both clusters consist of four silver atoms coordinated to four monoanionic ligands, two of them acting as [PS] bidentate and the other two as [PNS] tridentate. Although the two aggregates have the same composition, a careful comparison clear shows some connectivity differences. In both clusters, a and b, the external silver atoms [Ag(2A) (a); Ag(4) (b)] are coordinated to two ligand units. One of them is coordinated through a [PS] donor system, with the imine nitrogen atom remaining unbound. Nevertheless, the second ligand shows a different coordination pattern: in cluster a, the second strand is bound to the external silver atom [Ag(2A)a] using the three donor atoms and therefore acting as a [PNS] tridentate. On the contrary, in cluster b, the external silver atoms [Ag(4)] are coordinated to the second ligand unit via the sulfur and the imine nitrogen atoms, while the phosporous atom is coordinated to the contiguous internal silver center [Ag(3)]. This different coordination mode shown by two of the four ligand chains in the pair of clusters brings the internal silver atoms in cluster b [Ag(3)–Ag(3) 2.9418(4) Å] closer than those in
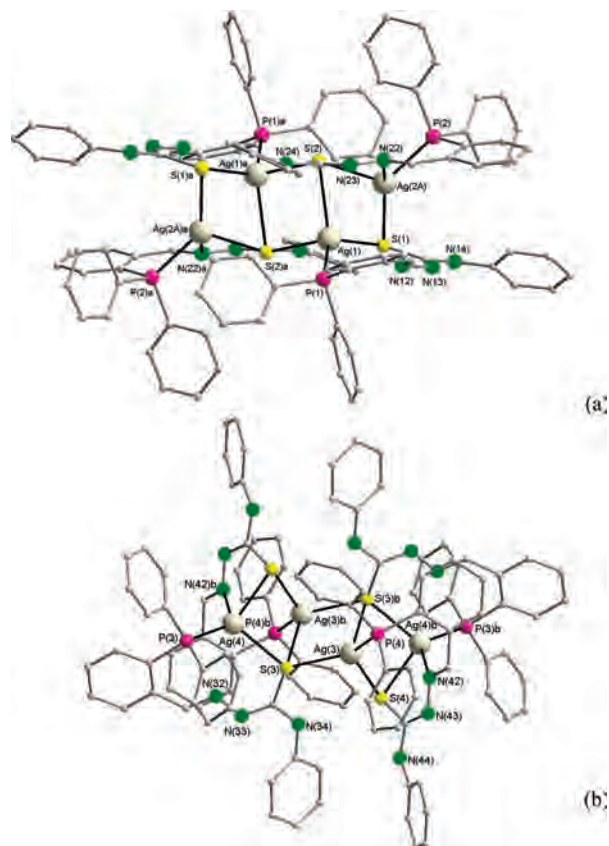

Figure 2. Representation of the [AgLPPh]$_4$^{a} cluster (a) and the [AgLPPh]$_4$^{b} cluster (b) with a labeling scheme for non-carbon atoms. For clarity, hydrogen atoms and solvent molecules have been omitted.

cluster a [Ag(1)–Ag(1) 3.627(5) Å]. As a consequence, the distances between external and internal atoms are smaller in cluster a [Ag(1)–Ag(2A) 2.9067(6) Å] compared with those in cluster b [Ag(3)–Ag(4) 3.0964(3) Å]. This coordination behavior establishes notable metal–metal interactions among Ag(4)–Ag(3)–Ag(3)–Ag(4) atoms in cluster b, although the existence of a formal bond cannot be considered because the Ag–Ag distances are smaller than twice the van der Waals radius for silver (3.44 Å).[14] In contrast, cluster a exhibits a stronger argentophilic interaction between the pairs Ag(1)–Ag(2A), with distances similar to those found on the metallic silver (2.889 Å).[15] Moreover, the internal distance Ag(1)–Ag(1) is larger than the sum of the van der Waals radii of two silver atoms, but a weak interaction cannot be discarded.

It is well-known that the presence of direct metal–metal interactions is one of the important factors contributing to the photoluminiscent properties of d^{10} metal compounds.[16] Nevertheless, until now, only a few silver(I) complexes have been reported to emit at room temperature,[17] because most of them only exhibit emission at low temperature.[18] Interestingly, the ligand HLPPh and its silver complex **1** are luminescent at room

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(13) [Ag$_4$(LPPh)$_4$]^a[Ag$_4$(LPPh)$_4$]^b·MeOH (**2**; C$_{108}$H$_{100}$Ag$_4$N$_{12}$O$_4$P$_4$S$_4$, M_w = 2313.60; crystal dimensions 0.55 × 0.28 × 0.08 mm^3, triclinic, $P\bar{1}$, a = 14.4071(3) Å, b = 16.1237(3) Å, c = 22.0432(5) Å, α = 87.1550(10)°, β = 86.7750(10)°, γ = 78.7520(10)°, V = 5010.33(18) Å^3, Z = 2, ρ_{calcd} = 1.534 mg/m^3, $F(000)$ = 2352. Radiation λ(Mo Kα) = 0.71073 Å, T = 100(2) K, reflections collected/unique 165 941/24 974 (R_{int} = 0.0310). R = 0.0378, wR = 0.0964, GOF = 1.043, max/min residual density 1.469/−1.178 e/Å^3. Cluster a contains two of the silver atoms disordered, Ag(2), which have been labeled as Ag(2A) and Ag(2B). Ag(2B) has not been depicted for clarity purposes. CCDC 675723.
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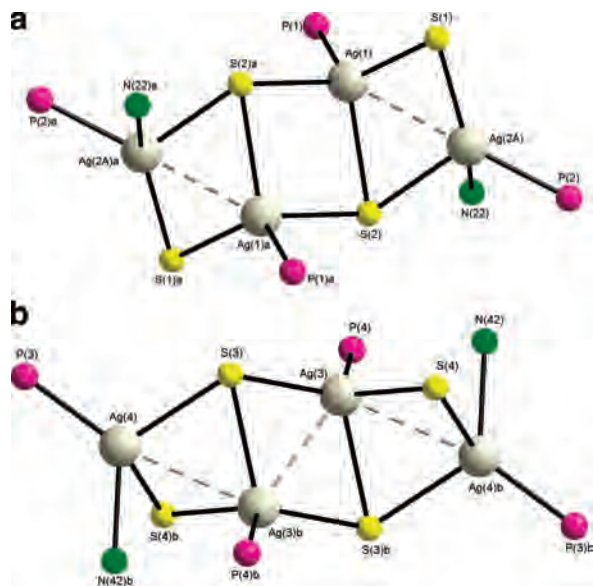
Figure 3. (a) Perspective representation of the $Ag_4N_2P_4S_4$ central core of cluster a, $[AgLPPh]_4{}^a$. Selected bond distances (Å): Ag(1)−P(1) 2.4505(8); Ag(1)−S(1) 2.5759(8); Ag(1)−S(2) 2.8079(8); Ag(1)−S(2)a 2.5822(7); Ag(2A)−P(2) 2.4084(10); Ag(2A)−S(1) 2.5095(8); Ag(2A)−S(2) 2.5645(14); Ag(2A)−N(22) 2.5645(14); Ag(1)−Ag(2A) 2.9067(6); Ag(1)−Ag(1)a 3.6275(5); S(1)−S(2) 4.1964(11); S(2)−S(2)a 3.9931(15). Symmetry transformations: a, −x + 1, −y + 1, −z + 1. (b) Perspective representation of the $Ag_4N_2S_4$ central core of cluster b, $[AgLPPh]_4{}^b$. Selected bond distances (Å): Ag(3)−P(4) 2.4660(9); Ag(3)−S(3) 2.5754(8); Ag(3)−S(4) 2.6590(9); Ag(3)−S(3)b 2.8111(8); Ag(4)−P(3) 2.4146(8); Ag(4)−S(3) 2.6953(8); Ag(4)−S(4)b 2.6037(8); Ag(4)−N(42)b 2.4424(26); Ag(3)−Ag(3)b 2.9418(5); Ag(3)−Ag(4)b 3.0965(3); S(3)−S(3)b 4.5184(15); S(3)−S(3)b 3.8811(8). Symmetry transformations: b, −x + 2, −y + 1, −z + 1.
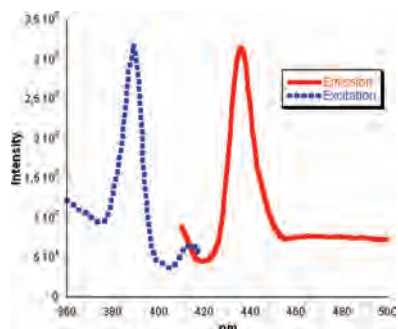

Figure 4. Emission (λ_{ex} = 390 nm) and excitation (λ_{em} = 436 nm) spectra in methanol (5 × 10^{-5} M) at room temperature for complex **1**.

temperature, in methanol solutions. The emission spectrum of the ligand HLPPh displays a single broad band with a maximum at ca. 472 nm (when it is excited at 328 nm). However, complex **1** shows a sharp intense emission with a maximum at 436 nm, upon excitation at λ = 390 nm (Figure 4). Additionally, the excitation spectrum of **1** essentially fits its absorbance, showing a Stokes shift of ca. 70 cm^{-1}. Compared with the ligand, the emission in complex **1** is shifted and notably enhanced. This enhancement can be ascribed to the silver cluster-based centers therein,[16] although other factors like increases of the conformational rigidity and the conjugation of charge after coordination could also contribute.[19] The origin of luminescence for d^{10} metal clusters seems to be highly dependent on the particular metal core features shown in the solid state.[8] In the case of halide-free tetranuclear square-planar clusters like a and b,

emission can be assigned to metal-centered 5d−6s transitions, while metal-to-ligand charge-transfer transitions are discarded because of the large Stokes shift value.[8] For the time being, it is difficult to determine the exact origin for the emission displayed by silver(I) thiosemicarbazone clusters because of the complexity brought by the metallophilic attractions[20] and the lack of luminiscence studies for these kinds of compounds.[4,6] For that reason, further work is necessary in this area.

The novelty of the two Ag_4 clusters reported herein resides in the unusual ligation-induced core arrangement obtained by using a thiosemicarbazone ligand bearing a phosphine moiety. Although some reports on silver(I) clusters containing different cores have been published,[4,5,7] the herein explained $Ag_4N_2S_4P_4$ a and b clusters are unique samples. On the basis of their structure and those previously reported,[4,5,7] some general trends about the coordinative factors involved in the cluster assembly can be drawn: (a) All of the structures demonstrate that the thiosemicarbazone must be deprotonated for the assembly of silver clusters. (b) The use of the three donor atoms in a tridentate thiosemicarbazone ligand, at least in two of the ligand units, gives rise to tetranuclear clusters rather than hexanuclear ones. (c) The introduction of phosphorus in the thiosemicarbazone, instead of hard donors like oxygen or nitrogen, does not prevent the formation of a tetranuclear cluster structure, but it affects the core microarchitecture. This effect is clearly shown by our silver clusters, which exhibit a new coordinative situation: the imine nitrogen atom remains unbound in two of the four ligands involved in the cluster structure and therefore tetranuclear clusters are assembled but use fewer donor atoms (10 in our $Ag_4N_2S_4P_4$ clusters versus 12 in $Ag_4N_8S_4$). (d) Coordination of all/some of the imine nitrogen atoms gives rise to silver tetranuclear cores. On the contrary, if all of them remain unbound and the hydrazide nitrogen atoms are coordinated instead, hexanuclear silver species should result. (e) Incorporation of bulky substituents (phenyl, morpholyl, etc.) at the thioamide nitrogen atom of the thiosemicarbazone seems to have a remarkable influence because tetranuclear clusters are exclusively formed.

In summary, we can conclude that the thiosemicarbazone structure (especially the number and nature of the donor atoms) is determinant in order to establish the nuclearity of the silver cluster assembled.

Supporting Information Available: Experimental and characterization details for ligand HLPPh and complex **1** and a CIF file for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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