1,5-Bis(benzothiazolyl)-3-thiapentane and its asymmetric dinuclear Ag(I) complex with three distinct intermolecular-stacking interactions†

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Synthesis of a dibenzothiazole thioether ligand that coordinates Ag(I) yielding an asymmetric dinuclear complex with three unique intermolecular π-stacking interactions, which influence the first coordination spheres of the silver centers, is reported.

Over recent years considerable effort has been directed towards the design and synthesis of new ligands to investigate π-stacking interactions for self-assembly or molecular recognition processes.[1–5] Previously, several (LAg)∞ networks have been reported as 2-D sheets or 3-D arrays held together by such intermolecular forces.[1–5] Herein we describe the synthesis and structure of an asymmetric, dinuclear Ag(I) complex with $[L_2Ag_2(NCCH_3)]^{2+}$ units ordered in a 'head-to-head' and 'tail-to-tail' network due to intermolecular π-stacking interactions.

The tritylated ligand precursor **1** was prepared from *S*-tritylated 2-aminothiophenol and 3,3′-thiodipropionic acid chloride analogous to the synthesis of 2,6-bis(tritylated amino-thiophenol)pyridylamide reported by Mascharak *et al.*[6] However, upon deprotection of the thiophenol *via* TFA and triethylsilane, **1** yields the unexpected product, 1,5-bis(benzothiazolyl)-3-thiapentane, **2**, as a white, crystalline solid, Scheme 1. Under the same reaction conditions, the pyridylamide derivative previously reported yields the deprotected thiolate. The benzothiazole ring likely results from the nucleophilic attack of the deprotected thiolate on the amide carbonyl with subsequent loss of water. In the pyridyl derivative, the amide carbonyl is expectedly less electrophilic due to electron delocalization over the pyridyl ring. Martell *et al.* have observed similar ring-forming reactions upon deprotection of imino-thiolate ligands.[7] Compound **2** was identified by NMR,‡ FT-IR, MS and X-ray crystallographic analysis.[8,9]

The mixed donor N/S donor set of **2** may potentially act as a versatile multidentate chelating ligand towards transition metal ions. Additionally, the thioether sulfur atoms are potential bridging donors, making it possible to assemble large molecules by careful selection of metal ions and counter anions.[11] These considerations encouraged us to study the chelating behavior of the ligand with the silver(I) ion. Reaction of **2** with $AgPF_6$ in a 1:1 molar ratio in CH_3CN–CH_2Cl_2 for 3 days afforded a pale-yellow solid, **3**, after removal of the solvents.[12] The ^{1}H NMR of the residue in CD_3CN displays a spectrum similar to that of **2** with resonances slightly shifted downfield in the silver complex. Recrystallization from CH_3CN–CH_2Cl_2 *via* hexane diffusion gave colorless crystals of **3**, suitable for X-ray diffraction analysis.[13] Crystals of **3** are composed of a discrete dinuclear cation, Fig. 1, as well as two PF_6 anions and a dichloromethane solvate molecule. The disilver cation contains two unique 4-coordinate silver(I) ions.
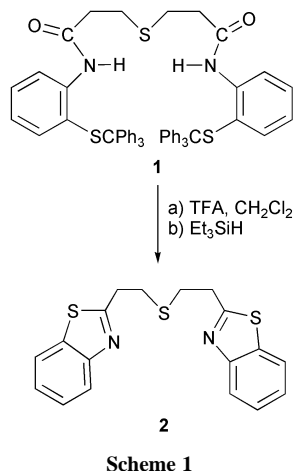
The Ag(1) ion is bound by 2 nitrogens and one sulfur from a single dibenzothiazole thioether ligand and by a bridging sulfur, S(5), from another equivalent of **2** in the unit cell. The geometry about Ag(1) is best described as distorted tetrahedral. The S(5)–Ag(1)–X angle to the other donor atoms is slightly distorted, 101.14(6)° for N(1), 107.14(6)° for N(2), and 114.96(2)° for S(2). However, the N(1)–Ag(1)–N(2) is significantly greater than expected, 144.77(8)°. Correspondingly, the S(2)–Ag(1)–N(1) and S(2)–Ag(1)–N(2) angles are slightly pinched, 89.66(6)° and 96.90(6)°, respectively. The Ag(1) to nitrogen bond distances, 2.274(2) Å and 2.225(2) Å for Ag(1)–N(1) and Ag(1)–N(2), are typical of tetrahedral Ag(I) complexes. The Ag–S distances to the terminal and the bridging thioether are quite comparable, Ag(1)–S(2), 2.597(1) Å and Ag(1)–S(5), 2.569(1) Å.

The geometry about Ag(2) is best described as 'see-saw like' or a 2 + 2 coordination.[14] The two nitrogen donors of the dibenzothiazole ligand are coordinated in the ″axial″ positions with a N(3)–Ag(2)–N(4) bond angle of 159.83(8)°. The Ag–N bond distances of 2.170(2) Å and 2.181(2) Å for Ag(2)–N(3) and Ag(2)–N(4), respectively, are slightly shorter than those observed for Ag(1). Likewise, the two 'equatorial' ligands display longer than expected metal–ligand bond distances of 2.553(3) Å for Ag(2)–N(5) and 2.8191(7) Å for Ag(2)–S(5). The acetonitrile is coordinated in a bent motif, Ag(2)–N(5)–
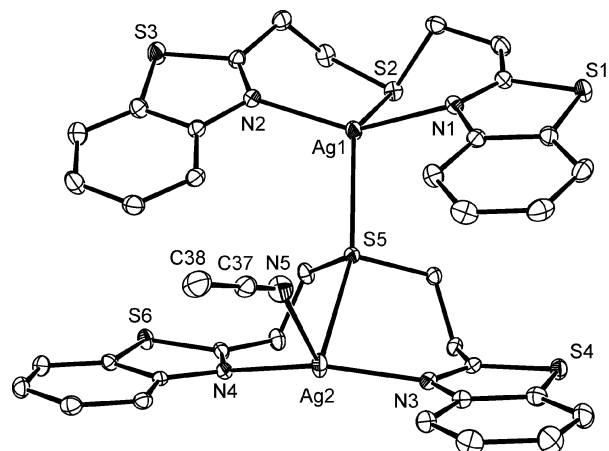

Scheme 1

a) TFA, CH₂Cl₂
b) Et₃SiH

Fig. 1 ORTEP[10] representation of the disilver cation of **3** showing 30% displacement ellipsoids. Hydrogen atoms are omitted.

† Electronic supplementary information (ESI) available: 3D rotatable structures of **2** and **3**. See http://www.rsc.org/suppdata/cc/b2/b204843d/

C(37) = 144.8(2)°, as observed in other sterically constrained Ag complexes.[15]

The disilver cations of **3** pack in a 3-D network *via* 'head-to-head' and 'tail-to-tail' interactions, Fig. 2. The Ag(2) centered 'heads' stack together with an offset, or slipped, overlap of 5- and 6-membered rings with the sulfurs of the five-membered rings, S6 and S4, centered under the six-membered ring of the neighboring ion. The sulfur to centroid distance is 3.57 Å for S4 and 3.51 Å for S6. The sulfur to centroid vector intersects the benzothiazole plane at an angle of 84.7°. The atypical geometry about Ag(2) is attributable to these π-stacking interactions, which sterically block one side of the silver coordination sphere and forces the acetonitrile molecule back towards the co-ordinated thioether yielding the observed N(5)–Ag(2)–S(5) bond angle of 93.39(6)°. In fact, the Ag(2) 'head-to-head' core has geometry reminiscent of bridging bidentate phosphines complexes with π-stacking interactions serving as the bridges, although the Ag(2)–Ag(2)′ intermolecular distance of 3.86 Å is too long for metal–metal bonding.[16]

The Ag(1) 'tails' of **3** aggregate in a zigzag pattern with alternating π-stacking interactions. The 5-membered rings of adjacent N(1) containing benzothiazole moieties overlap in an offset π-stack with the sulfur, S(1), positioned 3.64 Å directly under the centroid of the neighboring ring. The angle between the sulfur-centroid and centroid–centroid (4.03 Å) vectors of 21° is typical of nitrogen containing offset π-stacked rings.[3] The N(2) containing benzothiazole rings stack to a different neighboring cation than the N(1) containing ring. The N(2) rings overlap similar to the 'head' region except that the 6-membered portion of the ring lies above nitrogen, N(2), instead of sulfur with offset π-stacking of the 5- and 6-membered rings. The nitrogen to centroid vector is nearly perpendicular to the benzothiazole ring, 89.5° with a nitrogen to centroid distance of 3.43 Å. The two PF₆⁻ anions and one CH₂Cl₂ solvent molecule occupy channels on either side of the stacked cations with no fluoride or chloride intermolecular interactions.

In conclusions, we report a novel ring-forming reaction resulting from the nucleophilic attack of a thiolate sulfur on an amido-carbonyl yielding a new dibenzothiazole thioether. This ligand coordinates Ag(I) yielding an asymmetric dinuclear core with three distinct intermolecular π-stacking interactions. These interactions control the molecular geometry of the Ag(I) complex in the solid state.
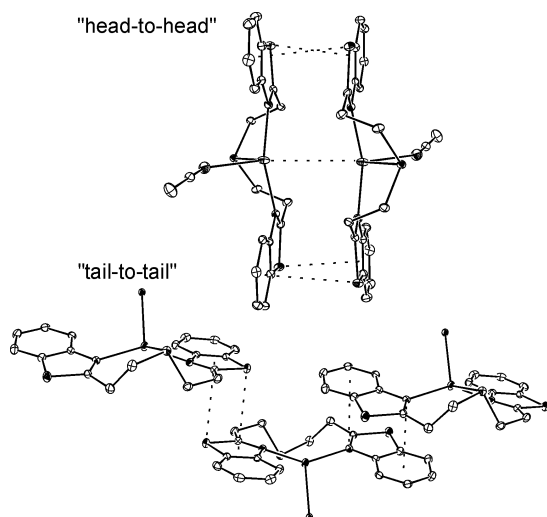
Fig. 2 View of the intermolecular π-stacking interactions of **3** associated with the Ag(2) centered 'head' with the Ag(1) 'tail' omitted (top) and the Ag(1) centered 'tail' with the Ag(2) 'head' omitted (bottom). Dashed lines indicate intermolecular distances described in the text.

Notes and references

‡ NMR spectra were recorded on a Varian Inova500 spectrometer. Infrared spectra were recorded as KBr disks on a Nicolet Avatar Spectrometer at 4 cm⁻¹resolution. ESI-mass spectra were recorded at the Biomolecular Mass Spectrometry Laboratory, University of Louisville. X-Ray data were collected on a Bruker Smart APEX CCD.[17]

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8 *Selected data* for **2**: ¹H NMR (CD₃CN, 500 MHz, 298 K): δ 3.14 (*t*, 4H, *J* = 7.0Hz), 3.44 (*t*, 4H, *J* = 7.0 Hz), 7.44 (*dd*, 2H, *J*₁ = *J*₂ = 8.0 Hz), 7.52 (*dd*, 2H, *J*₁ = *J*₂ = 8.0 Hz), 7.96 (*d*, 2H, *J* = 8.0 Hz), 7.98 (*d*, 2H, *J* = 8.0 Hz); ¹³C NMR (CDCl₃, 125 MHz, 298 K), δ 31.5, 34,.7, 121.8; 122.9, 125.4, 126.6, 135.1, 153.0, 169.7. MS(ESI) *m/z*: 357 (M⁺ + H).

9 *Crystal data* for **2**, C₁₈H₁₆N₂S₃: *M* = 256.51, monoclinic, space group *C*2/*c*, *a* = 31.066(4), *b* = 4.9437(6), *c* = 11.212(1) Å, β = 110.472(2)°, *V* = 1613.1(3) Å³, *T* = 100(2), λ = 0.71073 Å, *Z* = 4, μ(Mo-Kα) = 0.459 mm⁻¹, 6626 reflections measured, 1874 independent reflections (*R*ᵢₙₜ = 0.028), *R*₁ = 4.2%, *wR*₂ = 9.6% [*I* > 2σ(*I*)], *R*₁ = 5.0%, *wR*₂ = 9.9% (all data) GOF = 1.09. CCDC 186788.

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12 *Selected data* for **3**: ¹H NMR (CD₃CN, 500 MHz, 298 K): δ 3.19 (*t*, 4H, *J* = 7.0 Hz), 3.47 (*t*, 4H, *J* = 7.0 Hz), 7.51 (*dd*, 2H, *J*₁ = *J*₂ = 8.0 Hz), 7.58 (*dd*, 2H, *J*₁ = *J*₂ = 8.0 Hz), 8.03 (*d*, 4H, *J*₁ = *J*₂ = 8.0 Hz). IR bands (KBr pellets, cm⁻¹): 834 (*s*, PF₆), 2353 (*w*, CH₃CN). Calcd. for **3**·2H₂O: C, 33.97, H, 2.85, N, 5.08. Found: C, 33.87, H, 2.81, N, 4.44%.

13 *Crystal data* for **3**, C₃₉H₃₅N₅S₆Ag₂Cl₂P₂F₁₂: *M* = 1342.66, triclinic, space group *P*1̄, *a* = 13.408(1), *b* = 16.540(2), *c* = 13.188(1) Å, α = 77.625(2)°, β = 117.474(2)°, γ = 112.922(2)°, *V* = 2387.8(4) Å³, *T* = 100(2) K, λ = 0.71073 Å, *Z* = 2, μ(Mo-Kα) = 1.346 mm⁻¹, 21070 reflections measured, 10667 independent reflections (*R*ᵢₙₜ = 0.022), *R*₁ = 3.3%, *wR*₂ = 7.7% [*I* > 2σ(*I*)], *R*₁ = 4.4% and *wR*₂ = 7.9% (all data) GOF = 1.05. CCDC 186789. See http://www.rsc.org/suppdata/cc/b2/b204843d/ for crystallographic data in CIF or other electronic format.

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