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Supramolecular structures of $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2\}_\infty$: formation of argentamacrocycles and argentachains

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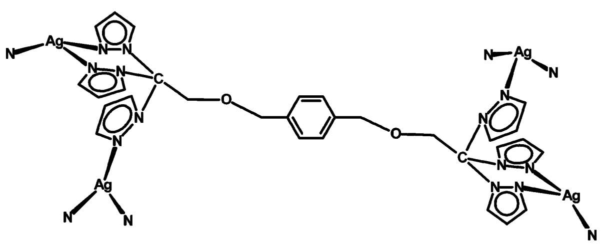
The coordination polymer $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2\text{-}(AgSbF_6)_2\}_\infty$ crystallizes into two supramolecular structures, one organized into a 3D structure of argentamacrocycles stacked in a tubular network connected by helically oriented organic spacers and the other into argentachains arranged in a 2D sheet structure.

Multidimensional networks based on coordination polymers are of interest because of their potential as functional materials.[1] To date, most coordination polymers have been prepared with rigid ligands,[2] but flexible ligands have also been employed.[3] We have designed a new class of multitopic ligands based on semi-flexible organic spacers of the general formula $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$, ($n$ = 2, 4; pz = pyrazolyl ring) that link two or more tris(pyrazolyl)methane units in a single molecule.[4] We have shown that metal complexes of these ligands form 2D and 3D supramolecular structures organized by non-covalent interactions, such as weak hydrogen bonds,[4a–c] intermolecular[4b] or intramolecular[4c,d] π–π stacking and C–H ··· π interactions.[4b] We report here that the bitopic ligand $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ reacts with $AgSbF_6$ to produce a compound,† when crystallized from acetone, of the formula $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2[(CH_3)_2CO]_2\}_\infty$ (**1**). In the solid state, **1** contains “argentamacrocycle” tubes linked in a unique 3D structure by helically oriented organic spacers. In contrast, crystallization from acetonitrile yields $\{[p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2(CH_3CN)_2]\}_\infty$ (**2**), that is shown to be a 2D coordination polymer containing “argentachains” rather than argentamacrocycles.

Crystals of **1** were grown by vapor phase diffusion of diethyl ether into an acetone solution. Single crystal X-ray analysis‡ showed that in **1** each tris(pyrazolyl)methane unit is κ[1] bonded to one silver(I) atom and κ[2] to another (Scheme 1 and Fig. 1a).[5]



Scheme 1 The κ[1]-κ[2] coordination mode of $[C(pz)_3]$ units in silver coordination polymers.

Six κ[1]-κ[2] $[C(pz)_3]$ units from six different bitopic ligands form a 36-member argentamacrocycle core with a AgNNCNN sequence, containing six silver ions, with no Ag ··· Ag interactions, the distance between two consecutive silver atoms being 5.54 Å. The argentamacrocycles are connected by the side arms of the organic spacer. The arms have a skewed *trans* arrangement with the angle formed by the arene ring and the plane of the attached CH_2OCH_2 group of 42.6°, an orientation that leads to a helical arrangement of the spacer along a crystallographic 3_1 screw axis (Fig. 1b).

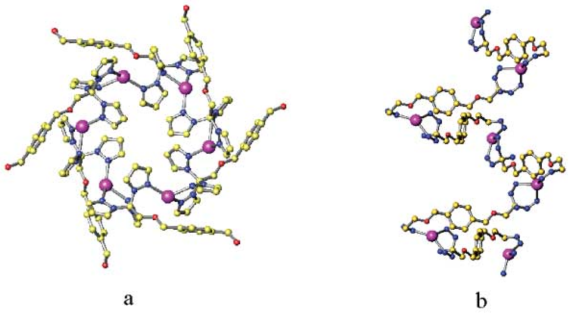


Fig. 1 a) The argentamacrocycle core of $\{p\text{-}C_6H_4[CH_2OCH_2C\text{-}(pz)_3]_2(AgSbF_6)_2[(CH_3)_2CO]_2\}_\infty$ (**1**) created by the κ[1]-κ[2] bonding mode of the tris(pyrazolyl)methane units; hydrogen atoms omitted, silver: purple, carbon: yellow, nitrogen: blue and oxygen: red. b) The helical arrangement of the spacer linking adjacent argentamacrocycle cores; each silver atom is part of a different macrocycle.

Each ligand has its $[C(pz)_3]$ units involved in two different argentamacrocycle cores such that every helical spiral is surrounded by three argentamacrocycle groups that are stacked along the c axis forming tubes with *ca.* 4 Å central cores (Fig. 2a). In the 3D structure, each argentamacrocycle tube is surrounded by six trigonally shaped helical spirals formed by the organic spacers and is connected by them to six other argentamacrocycle tubes.

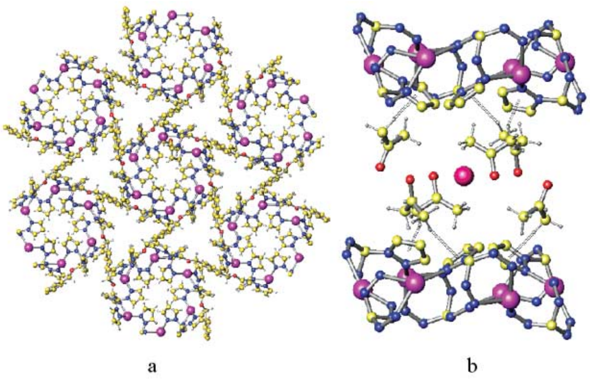


Fig. 2 a) The overall structure of **1**, SbF_6^- anions not shown, viewed down seven of the argentamacrocycle tubes connected by six trigonally shaped helical spirals. b) Two argentacrown cores and six acetone molecules surrounding an SbF_6^- anion for **1**, showing the C–H ··· π interactions between acetone and pyrazolyl rings as dotted lines. Only essential atoms are shown and the disordered fluorine atoms of the SbF_6^- group are omitted.

Fig. 2b shows the arrangement of two argentamacrocycles that make up the tubes. A pair interacts with six acetone molecules *via* short C–H ··· π interactions with the pyrazolyl rings within the argentamacrocycle cores, shown with dotted lines in the figure. The H–centroid distance is 2.47 Å (with a carbon–centroid distance of 3.35 Å), with the corresponding C–H–centroid angle of 149°. These values are typical for C–H ··· π interactions.[6] A striking feature of the structure is that in spite

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of the electron rich environment provided by the carbon–oxygen double bond from the acetone molecules and the π clouds from the pyrazolyl rings, one SbF_6^- anion (fluorines disordered) is between two argentamacrocycle cores. The remaining SbF_6^- anions (also disordered) are located within the helical arrangement of the spacer. An interesting feature of the structure brought out by Fig. 2b is that each argentamacrocycle "looks" like a crown compound and each pair acts as a "host" to a SbF_6^- and six acetone "guests". In this way **1** can be considered also as a metallacrown compound.[7] To the best of our knowledge, this structure represents the largest metallacrown observed to date, a 36-membered metallacrown.

When acetone was replaced by acetonitrile in the crystallization procedure, crystals of the formula $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2(CH_3CN)_2[(CH_3CN)_{0.25}(C_4H_{10}O)_{0.25}]\}_\infty$ [**2**·$(CH_3CN)_{0.25}(C_4H_{10}O)_{0.25}$] were obtained. Crystallographic studies§ revealed that the structure is again formed by κ^1-κ^2 coordination of the tris(pyrazolyl)-methane units and subsequently with the same AgNNCNN sequence, but in this case arranged in *argentachains* (Fig. 3a) rather than argentamacrocycles. The chains are linked by the spacer and arranged in a 2D sheet structure. The silver atoms have a distorted tetrahedral environment, with an acetonitrile molecule occupying the fourth coordination site. In Fig. 3b the sheets are oriented horizontally down the argentachains showing the linking spacers, with the sheets separated by the SbF_6^- anions. This structure is very similar to that previously reported for $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgBF_4)_2(CH_3CN)\}_\infty$.[4e]

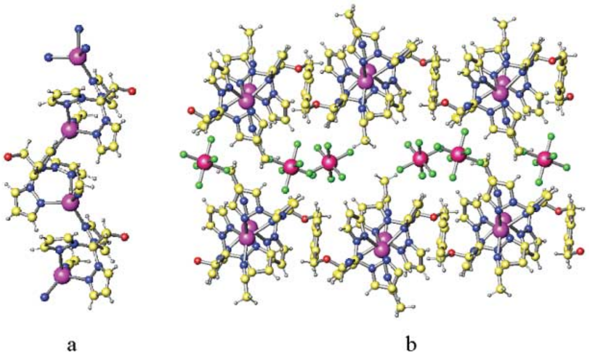

Fig. 3 a) One argentachain in $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2(CH_3CN)_2\}_\infty$ (**2**) built by a κ^1-κ^2 coordination of the $[C(pz)_3]$ units. b) Two sheets of **2** separated by the SbF_6^- anions.

In conclusion, the complex formed by the bitopic ligand $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ and $AgSbF_6$ forms, when crystallized from acetone/ether, a coordination polymer (**1**) comprised of 36-member argentamacrocycles stacked in a 3D network of tubes by helically oriented organic spacers. One SbF_6^- anion and six acetone molecules (guests) are located between each pair of argentamacrocycle cores (hosts). The solid, **2**, formed when the compound is crystallized from acetonitrile/ether has a structure based on argentachains held in a 2D sheet arrangement by the organic spacers with the counterions located between the sheets.

These two new supramolecular structures demonstrate that the bitopic $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ ligand is *structurally adaptive*, the presence of a coordinated solvent molecule leading to a dramatic change in structure. Such a ligand can adjust its structure to accommodate various reading algorithms of different metal systems and maximize non-covalent forces. With this ability to adjust to changes in the system, coupled with the ability to participate in π–π stacking and form C–H ··· π and weak hydrogen bonding interactions,[4] the $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ class of ligands based on linking tris(pyrazolyl)methane units with semi-rigid organic spacers are ideal candidates for studying the self-assembly process.

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Notes and references

† ^{1}H NMR (acetone-d$_6$) for **1**: δ: 7.82, 7.77 (m, 6,6H, 3,5-H *pz*), 7.09 (s, 4H, C_6H_4), 6.57 (d of d, 6H, *J* = 1.8 Hz, 4-H *pz*), 5.02 (s, 4H, $OCH_2C(pz)_3$), 4.67 (s, 4H, OCH_2Ph). Calc. for $C_{30}H_{30}Ag_2F_{12}N_{12}O_2Sb_2$: C, 28.20; H, 2.37; N, 13.15. Found C, 28.51; H, 2.21; N, 13.17%. ES$^+$/MS: *m*/*z* 699 and 1041, corresponding to $[LAg]^+$ and $[LAg_2SbF_6]^+$.

‡ Crystal data for $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2[(CH_3)_2CO]_2\}_\infty$ **1**: $C_{36}H_{42}Ag_2F_{12}N_{12}O_4Sb_2$, M = 1394.06, trigonal, a = 31.3014(18), c = 12.7921(11) Å, U = 10854.2(13) Å^3, T = 190(2) K, space group $R\bar{3}$, Z = 9, μ(Mo-Kα) = 2.005 mm^{-1}, 24083 reflections measured, 4922 unique (R_{int} = 0.0358), final R indices $[I > 2\sigma(I)]$: $R1$ = 0.0591, $wR2$ = 0.1794, R indices (all data): $R1$ = 0.0695, $wR2$ = 0.1885. CCDC reference number 191725.

§ Crystal data for $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(AgSbF_6)_2(CH_3CN)_2[(CH_3CN)_{0.25}(C_4H_{10}O)_{0.25}]\}_\infty$ **2**·$(CH_3CN)_{0.25}(C_4H_{10}O)_{0.25}$: $C_{35.50}H_{39.25}Ag_2F_{12}N_{14.25}O_{2.25}Sb_2$, M = 1388.80, triclinic, a = 10.4341(6), b = 15.4008(9), c = 15.8447(9) Å, α = 77.7240(10), β = 77.4120(10), γ = 78.3260(10)°, U = 2395.4(2) Å^3, T = 150(1) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 2.017 mm^{-1}, 22228 reflections measured, 9746 unique (R_{int} = 0.0291), final R indices $[I > 2\sigma(I)]$: $R1$ = 0.0339, $wR2$ = 0.0771, R indices (all data): $R1$ = 0.0420, $wR2$ = 0.0791. CCDC reference number 191728. See http://www.rsc.org/suppdata/dt/b2/b210819d/ for crystallographic data in CIF or other electronic format.

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