Beyond classical coordination: silver–π interactions in metal dipyrrin complexes

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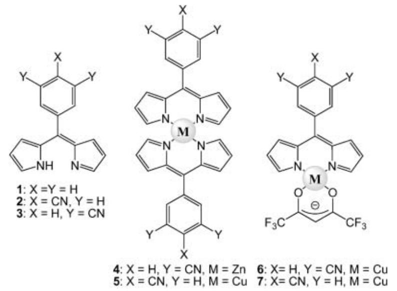
Homo- and hetero-leptic Zn and Cu complexes of dipyrrin type ligands bearing mono- and di-cyanophenyl groups when combined with silver cations lead to the formation of Ag(I)–C=C double bond interactions unprecedented in the crystalline phase.

The design and generation in the crystalline phase of infinite periodic self-assembled architectures called molecular networks is the subject of active research. In particular, coordination networks or Metal Organic Frameworks (MOFs), based on mutual bridging between organic and metallic tectons or building blocks, have attracted considerable interest because of their possible applications in gas storage, catalysis and magnetism.[1] Although numerous examples of homometallic coordination networks have been reported, the design and construction of heterometallic infinite architectures still remain a challenge.[2] The most viable approach for the formation of heterobimetallic networks (L,M1,M2) is the stepwise strategy which requires the presence, within the structure of the ligand ($L_{P1,P2}$), of two coordination poles P1 and P2 displaying different coordination propensities towards the metal centres M1 and M2. The design of such a system necessitates consideration of the (M1–P1) and (M2–P2) couples. Considering a hierarchy of interactions, P1 and P2 poles may be regarded as primary and secondary poles. Based on this idea, one may use dipyrrin derivatives decorated at the *meso* position with additional neutral coordination sites. Thus, owing to the anionic nature of the dipyrrin moiety under alkaline conditions, this chelate must behave as P1 whereas because of the neutral character of the peripheral coordinating unit the latter must act as P2. Since the reports by Lindsey[3a] and Dolphin[3b] on the synthesis of α,β-unsubstituted stable *meso*-functionalized dipyrrins such as compound **1** (Scheme 1) and its use as a ligand, the above mentioned design principle has been explored by Cohen *et al.* using the ligand **2**[4] (Scheme 1) bearing the benzonitrile moiety, as well as pyridine appended ligands and transition metals (M1) combined with silver cation (M2).[5]

We naively thought that the unreported ligand **3** (Scheme 1) based on a dipyrrin unit bearing two nitrile groups could be of interest for the generation of heterobimetallic coordination networks. Indeed, such a ligand should lead to the formation of a neutral tetrahedral Zn complex **4** (Scheme 1) offering four nitrile units as peripheral secondary coordinating sites. Assuming a linear coordination geometry, the combination of **4** with silver salts would, in principle, lead to the formation of a 3D coordination network of diamondoid type. However, this design principle relies on the absence of any other additional robust complexation events. We demonstrate herein that in addition to their reported coordination ability, nitrile functionalised dipyrrin metal complexes can also bind silver(I) centres *via* a Ag–π interaction. This is, to our knowledge, the first structural evidence of such an interaction with pyrrolic ligands and its generality for dipyrrin-based systems is discussed.



Scheme 1

The synthesis of **3** was achieved in 30% overall yield. Condensation of 3,5-dicyanobenzaldehyde[6] with neat pyrrole (40 equivalents) followed by purification (SiO_2, eluent CH_2Cl_2) afforded 5-(3,5-dicyanophenyl)dipyrromethane. This derivative was subsequently oxidized with DDQ in benzene–$CHCl_3$ (1 :1) and purified (SiO_2, eluent cyclohexane–AcOEt 9 : 1) yielding **3**.

Upon treatment of a $CHCl_3$ solution of **3** with 2.5 equivalents of $Zn(OAc)_2$ in MeOH and purification (SiO_2, eluent CH_2Cl_2), the zinc complex **4** was obtained in 32% yield. Dark-red crystals of **4** were grown by slow diffusion of pentane into a $CHCl_3$ solution of the complex. The structural study by X-ray diffraction† revealed that complex **4** crystallizes in the monoclinic space group *C*2/*c* with one complex on a 2-fold axis (Fig. 1), as reported for the zinc complex of ligand **1**.[7a] The Zn^{2+} cation adopts a tetrahedral coordination geometry with dihedral angle of 83.0° between the two dipyrrin units. The bond distances observed are similar to those reported for other Zn dipyrrin complexes (see Fig. 1).[7]

In order to generate the heterobimetallic network, the Zn(II) complex **4** was combined with Ag^+ cations. Slow evaporation of a

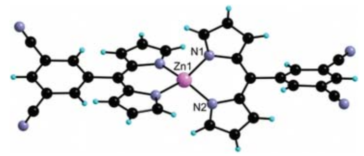


Fig. 1 View of **4**. Selected bond distances (Å) and angle (°): Zn1–N1, 1.9797(17); Zn1–N2, 1.9715(18) Å; N1–Zn1–N2, 95.62(7).

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benzene solution containing both the neutral zinc complex **4** and two equivalents of AgOTf afforded orange crystalline plates which were analyzed by X-ray diffraction. The crystal (monoclinic, $P2_1/n$) is composed of **4** and silver cations, triflate anions and benzene molecules (**4**(AgOTf)$_2$(C$_6$H$_6$)$_{2.5}$). Two crystallographically non-equivalent silver cations (Ag1 and Ag2) and ligands **3** are present in the unit cell. Among the three benzene molecules, two are in general positions and one is lying on an inversion centre.† Surprisingly, the silver cations are not only bound to the nitrile groups and the triflate ions, as one would expect, but interact also with the C=C double bonds of the pyrrole groups (C2=C3) of the dipyrrin unit (Fig. 2). Taking into account this interaction, the overall structure is a 2D network. The Ag–C distances are in the usual range observed for η^1 and η^2 arene–silver complexes and the complexation is unsymmetrical with one Ag–C contact longer than the other (Fig. 2).[8] The distances of the two silver atoms from the mean plane of the coordinated pyrrole of 2.314 and 2.327 Å for Ag1 and Ag2 respectively are slightly shorter than the average distance of 2.41 Å reported by Kochi *et al.* in the case of arenes.[8d]

Although Ag(I)–π interactions have been previously observed with arenes,[8] such interactions with dipyrrin units in the solid state have not been documented in the literature. However, in solution, based on NMR, UV-Vis and Raman investigations, this type of interaction has been postulated for the binding of Ag(I) by an allosteric system based on a Ce(IV) double-decker porphyrin.[9] The observation in the solid state reported here strongly supports the proposed mechanism for the allosteric system reported by Shinkai *et al.*[9]

One might wonder whether complex **4** presents any peculiarity making it especially prone to Ag$^+$–π interaction. There are two aspects to this question: the role of the metal centre used to form the precursor such as complex **4** and the nature of the ligand **3**. In order to address the first part, the heteroleptic Cu(II) complex **6** composed of the ligand **3** and hexafluoroacetylacetonate (hfac) has been prepared as described for other such complexes[10] and reacted with silver cations to afford crystalline material. Again, the solid state investigation by X-ray diffraction revealed the same type of silver–π interaction. Unfortunately owing to low quality data, the structure is not reported here. These observations however clearly demonstrate that zinc does not seem to be the sole trigger of this interaction.

Considering the role of ligand **3**, one might argue that the observed interaction is related to electronic factors resulting from the presence of two nitrile groups at positions 3 and 5. In order to investigate this aspect, we have prepared complex **5**, analogue of complex **4**, for which the Zn(II) is replaced by Cu(II) and the ligand **3** by **2** (Scheme 1). This compound, although already reported in the literature,[10a] has to our knowledge not been associated with silver cations. Slow evaporation of a benzene solution of a stoichiometric mixture of **5** and AgOTf led to the formation of small red crystals. The crystal, (**5**)(AgOTf)$_2$(H$_2$O), (triclinic, $P\bar{1}$) is composed of one complex **5**, two silver cations, two triflate anions and one water molecule in general positions.† The two independent Ag$^+$ cations interact with nitrile groups and triflate anions as well as with the same C=C bonds of the dipyrrin ligands as observed with complex **4** (Fig. 3). The first silver cation, Ag1, is hexacoordinated as it is bound to one CN group, an oxygen atom of a OTf$^-$, and two C=C bonds belonging to two different copper complexes with distances to the mean plane of the pyrroles of 2.394 and 2.445 Å. The second cation, Ag2, also hexacoordinated, is bound to one nitrile group, two oxygen atoms of a triflate, one water molecule and two carbon atoms of a C=C bond with a distance to the mean plane of the pyrrole of 2.465 Å. The Ag–C distances are similar to the ones observed in the case of the zinc species described above. When considering this interaction, the overall arrangement is a 1D network. Note that the copper center is pentacoordinated as it is bound to the two dipyrrin chelates ($d_{\text{Cu–N}}$ = 1.971(9) Å) as well as to one of the oxygen atoms of a triflate anion ($d_{\text{Cu–O}}$ = 2.741(9) Å).

Furthermore, the heteroleptic Cu(II) complex **7** composed of the ligand **2** bearing a single nitrile group and hfac anion was also prepared[10] and reacted with silver salts under the same experimental conditions. High-quality single crystals were obtained in the presence of Ag(OTf) which were characterized by X-ray diffraction.† The crystal is composed of one Cu complex **7**, one silver cation, one triflate anion and one benzene solvate molecule in general positions and of one additional benzene molecule on an inversion centre (**7**(AgOTf) (C$_6$H$_6$)$_{1.5}$). The Ag(I), coordinated to one nitrile group and the triflate anion, again interacts with two pyrrole C=C double bonds of two Cu complexes **7** (Fig. 4). As presented above, the silver complexation is unsymmetrical with one Ag–C distance shorter than the other. The Ag–pyrrole mean plane distances are 2.342 and 2.499 Å, similar to those described

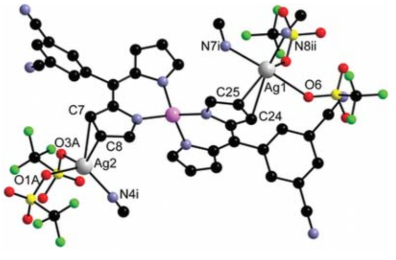

Fig. 2 Silver–π interaction in **4**(AgOTf)$_2$(C$_6$H$_6$)$_{2.5}$. Hydrogen atoms and benzene solvate molecules have been omitted for clarity. Only the nitrile groups of coordinated complexes **4** are shown. Selected bond distances (Å): Ag1–C24, 2.554(4); Ag1–C25, 2.488(4); Ag1–N7i, 2.438(4); Ag1–N8ii, 2.335(4); Ag1–O4, 2.379(3); Ag1–O6, 2.605(4); Ag2–C7, 2.583(4); Ag2–C8, 2.397(4); Ag2–N4i, 2.240(3); Ag2–O1A, 2.363(6); Ag2–O3A, 2.341(6); C7–C8, 1.394(6); C24–C25, 1.392(6). i = x, 1 + y, z; ii = 2 − x, 1 − y, 2 − z.

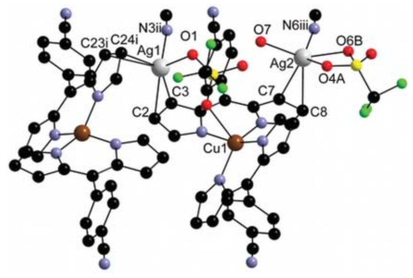

Fig. 3 Silver–π interaction in **5**(AgOTf)$_2$(H$_2$O). Hydrogen atoms as well as the disorder of one triflate anion have been omitted for clarity. Only the nitrile groups of coordinated complexes **5** are shown. Selected bond distances (Å): Ag1–C2, 2.558(10); Ag1–C3, 2.519(10); Ag1–C23i, 2.676(10); Ag1–C24i, 2.515(9); Ag1–N3ii, 2.330(8); Ag1–O1, 2.406(8); Ag2–C7, 2.637(10); Ag2–C8, 2.560(10); Ag2–N6iii, 2.246(8); Ag2–O4A, 2.39(2); Ag2–O6B, 2.314(17); Ag2–O7, 2.343(8); C2–C3, 1.381(13); C7–C8, 1.395(13); C23–C24, 1.387(13). i = 1 − x, 1 − y, 1 − z; ii = −x, 2 − y, 1 − z; iii = −1 + x, 1 + y, z.

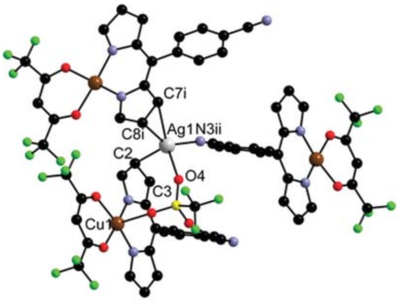

Fig. 4 Silver coordination environment in **7**(AgOTf) $(C_6H_6)_{1.5}$. Hydrogen atoms and benzene molecules have been omitted for clarity. Selected bond distances (Å): Ag1–C2, 2.536(5); Ag1–C7i, 2.703(5); Ag1–C8i, 2.382(5); Ag1–N3ii, 2.215(5); Ag1–O4, 2.450(4); C2–C3, 1.373(7); C7–C8, 1.388(7). i = x, 3/2 − y, 1/2 + z; ii = −x, 1 − y, −z.

above for the Zn and Cu complexes. By considering all types of interaction, the final architecture is a 2D network. Note that the triflate anion completes the coordination sphere of the Cu cation ($d_{Cu–O}$ = 2.400(6) Å) and is bound to Ag^+ ($d_{Ag–O}$ = 2.450(4) Å), thus locking the two metal centres together.

It is rather interesting to note that, although several heterobimetallic coordination networks based on the combination of the ligand **2** as well as other pyridine appended dipyrrins with various transition metals and silver salts have been reported,[5] this type of interaction has not been described before. This is probably due to the fact that these networks incorporate octahedral Co(III) and Fe(III) complexes.[5] For these species, the pyrrole C=C double bonds are less accessible and therefore for steric reasons only silver–nitrile coordination is observed. Finally, in order to study the effect of the presence of the nitrile group on the occurrence of the Ag(I)–π interaction, the homoleptic zinc complex of the ligand **1** was prepared according to reported procedure.[7a] Unfortunately, no suitable crystals could be obtained so far in the presence of AgOTf.

In conclusion, to the best of our knowledge, we have demonstrated the first structural evidence for a Ag(I)–π interaction taking place in the crystalline phase between silver cations and functionalised dipyrrin complexes. It appears that this interaction is robust and occurs with different dipyrrin based ligands (**2** and **3**) and their complexes (Zn, Cu). In terms of the design of heterobimetallic coordination networks based on dipyrrin derivatives bearing additional peripheral coordination sites such as nitrile groups, ligands **2** and **3** do not behave, as we naively envisaged, as coordinating construction units offering two differentiated coordination poles ($L_{P1,P2}$). In fact, these ligands are of the type ($L_{P1,P2,P3}$) as they display three coordination poles P1 (dipyrrin), and P2 (nitrile) and P3 (pyrrole C=C double bond) in the presence of transition metals and silver cations. Further investigations on the combination of ligands **1** and **2**, analogues and porphyrin derivatives with other metal centres and complexes and silver salts is currently under way in our laboratory and will be published in due course.

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Notes and references

† Crystal data for **4**: $C_{34}H_{18}N_8Zn$, M = 603.96, monoclinic, space group $C2/c$ (No. 15), a = 21.2112(12), b = 8.9839(5), c = 15.8267(9) Å, β = 111.097(2)°, V = 2813.8(3) Å^3, T = 173(2) K, Z = 4, D_c = 1.426 g cm^{-3}, μ = 0.913 mm^{-1}, 8704 collected reflections, 3215 independent (R_{int} = 0.0428), GooF = 1.026, R_1 = 0.0392, wR_2 = 0.0888 for $I > 2\sigma(I)$ and R_1 = 0.0639, wR_2 = 0.0974 for all data. Crystal data for **4**$(AgOTf)_2(C_6H_6)_{2.5}$: $C_{51}H_{33}Ag_2F_6N_8O_6S_2Zn$, M = 1313.08, monoclinic, space group $P2_1/n$ (No. 14), a = 17.9768(4), b = 10.3321(3), c = 28.9049(7) Å, β = 106.9440(10)°, V = 5135.7(2) Å^3, T = 173(2) K, Z = 4, D_c = 1.698 g cm^{-3}, μ = 1.380 mm^{-1}, 48 751 collected reflections, 15 035 independent (R_{int} = 0.0515), GooF = 1.023, R_1 = 0.0501, wR_2 = 0.1267 for $I > 2\sigma(I)$ and R_1 = 0.1022, wR_2 = 0.1543 for all data. Crystal data for **5**$(AgOTf)_2(H_2O)$: $C_{34}H_{22}Ag_2CuF_6N_6O_7S_2$, M = 1083.98, triclinic, space group $P\bar{1}$ (No. 2), a = 11.6021(5), b = 12.7762(5), c = 13.9264(5) Å, α = 64.995(2), β = 86.600(2), γ = 84.435(2)°, V = 1861.63(13) Å^3, T = 173(2) K, Z = 2, D_c = 1.934 g cm^{-3}, μ = 1.807 mm^{-1}, 30 358 collected reflections, 8318 independent (R_{int} = 0.0582), GooF = 1.074, R_1 = 0.0833, wR_2 = 0.2103 for $I > 2\sigma(I)$ and R_1 = 0.1478, wR_2 = 0.2666 for all data. Crystal data for **7**$(AgOTf)(C_6H_6)_{1.5}$: $C_{31}H_{20}AgCuF_9N_3O_5S$, M = 888.97, monoclinic, space group $P2_1/c$ (No. 14), a = 17.5627(6), b = 12.7625(4), c = 15.5101(5) Å, β = 107.838(2)°, V = 3309.37(19) Å^3, T = 173(2) K, Z = 4, D_c = 1.784 g cm^{-3}, μ = 1.393 mm^{-1}, 29 318 collected reflections, 7557 independent (R_{int} = 0.0564), GooF = 1.029, R_1 = 0.0525, wR_2 = 0.1484 for $I > 2\sigma(I)$ and R_1 = 0.0950, wR_2 = 0.1790 for all data. CCDC 641388–641391. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704466f

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