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Many Faces of Dipyrrins: from Hydrogen-Bonded Networks to Homo- and Heteronuclear Metallamacrocycles

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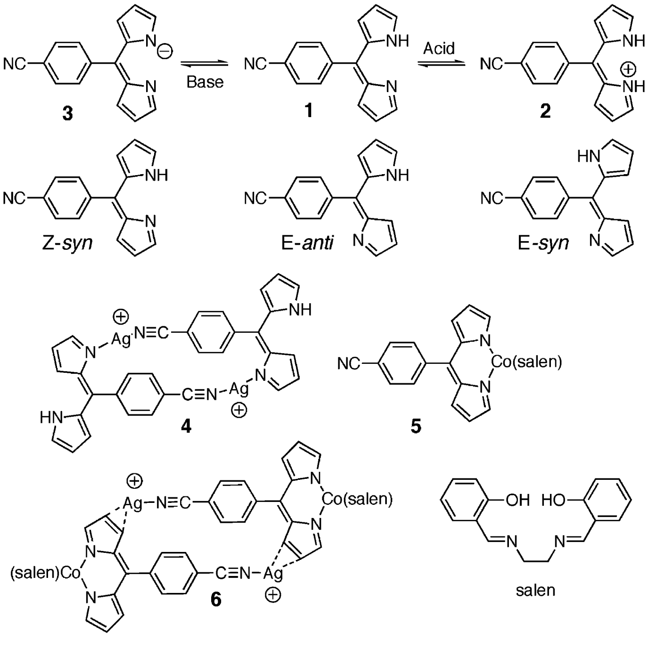
The amphoteric 5-(4-cyanophenyl)dipyrrin ligand, offering three distinct states, i.e., cationic, neutral, and anionic, has been exploited for the formation of a 1-D hydrogen-bonded network in its protonated form and both homo- and heterobinuclear metallamacrocycles, in its neutral and deprotonated states, respectively, with a variety of coordination modes.

Dipyrrins or dipyrromethenes (dpm) are bispyrrolic ligands attracting considerable interest over the past few years.[1] In particular, luminescent[2] as well as porous[3] materials based on dpm derivatives have been reported. Owing to the coexistence of both conjugated imine and amine functionalities, the dpm core presents an amphoteric character and may undergo two acid–base equilibria, leading to three distinct states (neutral **1**, cationic **2**, and anionic **3**), as depicted in Scheme 1. Furthermore, when considering the relative disposition of the two pyrrolic N atoms, dpm-type molecules may exist in three configurations (*Z*-syn, *E*-anti, and *E*-syn). In principle, the dpm moiety should behave as a hydrogen-bond donor[4] in its cationic protonated form, whereas in its neutral state, it would exhibit an ambivalent nature by behaving either as a hydrogen-bond acceptor and/or donor or as a coordinating group. Finally, in its anionic state resulting from its deprotonation, the dpm core should act as a chelate for the binding of metal centers. This latter feature has been extensively used for the formation of many metal complexes.[3,5] Dipyrrin derivatives, bearing additional coordinating groups at their periphery, have been used for the preparation of heterometallic architectures with Ag^+ cations.[3] Recently, it has been demonstrated in the solid state that, in addition to classical coordination, this type of species can bind Ag^+ cation via $Ag-\pi$ interactions taking place with the $C{=}C$ bond of the pyrrolic ring.[6] This type of interaction had been observed before in solution[7] and utilized for NMR and mass spectrometry studies of dpm derivatives.[8]

Scheme 1



In this contribution, we demonstrate the use of all three states (cationic, neutral, and anionic) of the dpm-based molecule **1**[9] in the generation of an infinite 1-D hydrogen-bonded network as well as in the formation of both homo- and heteronuclear metallamacrocycles.

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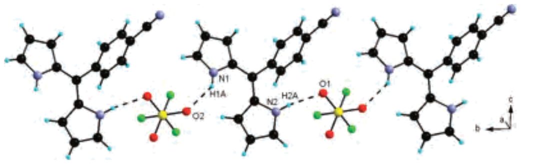

Figure 1. Formation of a 1-D hydrogen-bonded network between **2** and a OTf$^-$ anion. Selected bond lengths (Å) and angles (deg): N1−O2, 2.876(3); N2−O1, 2.936(3); N1−H1A−O2, 141.4; N2−H2A−O1, 161.6.

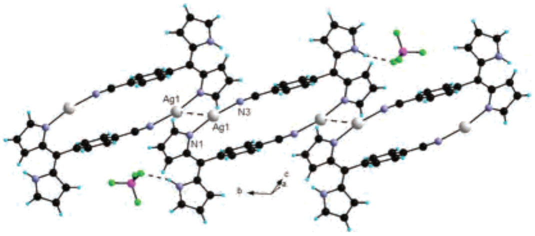

Figure 2. 1-D arrangement along the *b* axis of the metallamacrocycle $[Ag_2(\mathbf{1})_2]^{2+}$ **4**. Selected bond lengths (Å) and angles (deg): Ag1−N1, 2.138(3); Ag1−N3, 2.125(3); Ag1−Ag1, 3.396(4); N1−Ag1−N3, 169.3(1).

Upon reaction of **1**[9] with 1 equiv of trifluoromethanesulfonic acid (HOTf) in CH_2Cl_2, salt $(\mathbf{1}H)^+(OTf)^-$, **2** as a OTf$^-$ salt, is formed.[10a] Single crystals of the latter were prepared by diffusion of diethyl ether vapors into a solution of **2** in $CHCl_3$. The salt **2** crystallizes in the monoclinic space group $P2_1/c$ with one protonated ligand **1**-H$^+$ and one OTf$^-$ anion in general positions.[11a] In contrast with what was reported for salts of protonated 5-(pentafluorophenyl)-dipyrrin,[4] the two protonated pyrrolic rings in **2** are arranged in the *E*-anti configuration. The two pyrrolic rings are not coplanar but tilted with an angle of 19.1°. Both N−H groups are involved in hydrogen bonds (N−O distance in the range of 2.87−2.93 Å) with O atoms of OTf$^-$ anions, leading thus to the formation of a 1-D hydrogen-bonded network along the *b* axis resulting from the mutual interconnection between cations and anions (Figure 1).

The propensity of **1** to bind Ag$^+$ cations was investigated using $AgBF_4$. Upon slow evaporation of a benzene solution containing both **1** and $AgBF_4$, red crystals of a 2:2 complex $[(\mathbf{1})_2Ag_2](BF_4)_2$ (**4**; Figure 2) were formed and characterized by single-crystal X-ray diffraction and by elemental analysis.[10b,11b] The homobinuclear silver complex is, in fact, a dicationic 2 + 2 metallamacrocycle resulting from the bridging of two ligands **1** by two Ag$^+$ cations. The latter is linearly coordinated to one nitrile group and one unprotonated pyrrole nitrogen of the dpm moiety with the expected distances for such a coordination. This is one of the rare examples of a complex in which the neutral dpm does not act as a chelate.[12] As for the protonated form **2**, the dpm moiety adopts the *E*-anti arrangement. Within the macrocycle, although the Ag$^+$ cation is facing a phenyl ring, the shortest Ag−C$_{phenyl}$ distances of 3.019(4) and 3.035(4) Å suggest a rather weak interaction.[13] Interestingly, the metallamacrocycles are connected into a 1-D network along the *b* axis via a $d^{10}-d^{10}$ interaction,[14] with a distance of 3.396(4) Å between Ag$^+$ cations belonging to consecutive units. The remaining uncoordinated pyrrole ring forms hydrogen bonds with the BF_4^- anions [N−H−F, 2.871(4) Å, 160.3(2)°].

During this investigation, the formation of new heteroleptic complexes using the ligand **1** has also been studied. Salen

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(10) (a) Salt **2**: To a solution of **1** (0.08 g 0.32 mmol) in CH_2Cl_2 (20 mL) was added HOTf (28 μL, 0.32 mmol) in CH_2Cl_2 (20 mL). After stirring for 20 min at room temperature, the solvent was evaporated under reduced pressure to afford a dark residue in quantitative yield. Dark-red crystals were grown by slow diffusion of diethyl ether vapor into a $CHCl_3$ solution of the compound. ^1H NMR (300 MHz, acetone-d_6): δ 7.00 (br s, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.5$ Hz, 2H), 8.30 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.7, 116.0, 117.7, 119.7, 126.7, 129.3, 132.3, 132.6, 133.9, 143.9, 149.9. ^{19}F NMR (280 MHz, acetone-d_6): δ −79.3. IR (KBr/cm^{-1}): ν_{CN} 2242. (b) Complex **4**: A 1.75 mM solution of **1** in benzene (0.5 mL) was combined with a 1.75 mM solution of $AgBF_4$ in benzene (0.5 mL). Benzene was added (0.75 mL). Slow evaporation of the solution afforded orange crystalline platelets (yield ca. 25%). IR (KBr/cm^{-1}): ν_{CN} 2241. Anal. Calcd for $C_{32}H_{22}Ag_2B_2F_8N_6$: C, 43.68; H, 2.52; N, 9.55. Found: C, 44.10; H, 2.75; N, 9.60. (c) Complex **5**: A solution of **1** (0.1 g, 0.41 mmol) in $CHCl_3$ (22 mL) was treated with a solution of (salen)Co•H_2O (0.13 g, 0.41 mmol) in MeOH (10 mL). The mixture was stirred at room temperature for 45 min. Thin-layer chromatography analysis showed no remaining free dipyrrin. Purification by column chromatography (SiO_2; cyclohexane/AcOEt, 60/40) and recrystallization by slow diffusion of Et_2O vapors into a $CHCl_3$ solution of the complex afforded dark crystals of $(\mathbf{5})(CHCl_3)_2$ (90 mg, 27%). ^1H NMR (300 MHz, acetone-d_6): δ 2.66 (m, 1H), 3.46 (m, 1H), 3.81 (m, 1H), 4.15 (m, 1H), 6.16 (dd, $J^3 = 4.4$ Hz, $J^4 = 1.4$ Hz, 1H), 6.30 (m, 2H$_c$), 6.52 (m, 1H), 6.57 (dd, $J^3 = 4.4$ Hz, $J^4 = 1.3$ Hz, 1H$_d$), 6.60 (dd, $J^3 = 4.2$ Hz, $J^4 = 1.3$ Hz, 1H$_{d'}$), 6.82 (s, 1H), 6.95 (m, 2H), 7.01 (m, 1H), 7.20 (m, 2H$_e$), 7.43 (dd, $J^3 = 8.0$ Hz, $J^4 = 1.7$ Hz, 1H), 7.47 (s, 1H), 7.65 (d, $J = 8.4$ Hz, 2H$_a$), 7.78 (m, 1H, C−H), 7.91 (d, $J = 8.4$ Hz, 2H$_b$), 8.4 (s, 1H, C−H). ^{13}C NMR (75 MHz, acetone-d_6): δ 60.2, 60.6, 112.9, 114.0, 116.9, 118.6, 123.2, 123.5, 131.0, 131.4, 132.4, 132.4, 133.4, 134.8, 153.1, 158.5, 165.3, 166.6. UV−Vis (CH_2Cl_2; λ_{max}/nm (log ϵ): 272 (4.80), 302 (4.49), 399 (4.19) 483 (4.28), 512 (4.38). IR (KBr/cm^{-1}): ν_{CN} 2226, 1622. Anal. Calcd for $C_{34}H_{26}Cl_6CoN_5O_2$: C, 50.52; H, 3.24; N, 8.66. Found: C, 50.17; H, 2.93; N, 8.76. (d) Complex **6**: A 1.75 mM solution of complex **5** with benzene (0.5 mL) was combined with a 1.75 mM solution of $AgSbF_6$ in benzene (0.5 mL). This mixture was further diluted with benzene (0.75 mL) and acetonitrile (0.5 mL) and slowly evaporated to afford red crystals (yield ca. 32%). IR (KBr/cm^{-1}): ν_{CN} 2230. Anal. Calcd for $C_{68}H_{58}Ag_2Co_2F_{12}N_{12}O_6Sb_2$: C, 42.00; H, 3.01; N, 8.64. Found: C, 39.92; H, 2.96; N, 8.33.

(11) (a) Crystal data for **2** ($C_{17}H_{12}F_3N_3O_3S$): $M_W = 395.36$, monoclinic, $P2_1/c$, $a = 10.0624(6)$ Å, $b = 10.3247(6)$ Å, $c = 16.6996(9)$ Å, $\beta = 91.463(2)°$, $V = 1734.2(2)$ Å^3, $Z = 4$, $D_{calc} = 1.514$, $T = 173(2)$ K, $\mu = 0.241$ mm^{-1}, 15 368 reflns measd, 3972 unique reflns ($R_{int} = 0.0344$), $R = 0.0431$ [$I > 2\sigma(I)$], $R_w = 0.1279$ (for all data). (b) Crystal data for **4** ($C_{32}H_{22}Ag_2B_2F_8N_6$): $M_W = 879.92$, triclinic, $P\bar{1}$, $a = 9.9210(6)$ Å, $b = 10.0826(4)$ Å, $c = 10.1108(4)$ Å, $\alpha = 118.576(2)°$, $\beta = 100.160(3)°$, $\gamma = 108.078(3)°$, $V = 777.79(6)$ Å^3, $Z = 1$, $D_{calc} = 1.879$, $T = 173(2)$ K, $\mu = 1.343$ mm^{-1}, 8618 reflns measd, 3388 unique reflns ($R_{int} = 0.0373$), $R = 0.0339$ [$I > 2\sigma(I)$], $R_w = 0.0837$ (for all data). (c) Crystal data for $\mathbf{5}(CHCl_3)_2$ ($C_{34}H_{26}Cl_6CoN_5O_2$): $M_W = 808.23$, orthorhombic, $Pna2_1$, $a = 11.7199(8)$ Å, $b = 18.0162(13)$ Å, $c = 16.3131(11)$ Å, $V = 3444.5(4)$ Å^3, $Z = 4$, $D_{calc} = 1.559$, $T = 173(2)$ K, $\mu = 1.004$ mm^{-1}, 16 121 reflns measd, 6351 unique reflns ($R_{int} = 0.0531$), $R = 0.0603$ [$I > 2\sigma(I)$], $R_w = 0.1802$ (for all data). (d) Crystal data for **6** ($C_{68}H_{58}Ag_2Co_2F_{12}N_{12}O_6Sb_2$): $M_W = 1944.36$, monoclinic, $P2_1/c$, $a = 13.9626(5)$ Å, $b = 11.4836(4)$ Å, $c = 22.1003(8)$ Å, $\beta = 94.170(1)°$, $V = 3534.2(2)$ Å^3, $Z = 2$, $D_{calc} = 1.827$, $T = 173(2)$ K, $\mu = 1.847$ mm^{-1}, 27 280 reflns measd, 8122 unique reflns ($R_{int} = 0.0433$), $R = 0.0355$ [$I > 2\sigma(I)$], $R_w = 0.1107$ (for all data). (e) Crystallographic data were collected on a Bruker SMART CCD diffractometer with Mo Kα radiation. The structures were solved using *SHELXS-97* and refined by full-matrix least squares on F^2 using *SHELXL-97*. The H atoms were introduced at calculated positions and not refined (riding model).

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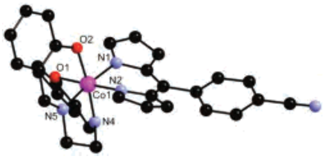

Figure 3. Structure of the heteroleptic cobalt complex **5**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−N1, 1.950(6); Co1−N2, 1.938(5); Co1−N4, 1.898(6); Co1−N5, 1.901(6); Co1−O1, 1.905(4); Co1−O2, 1.900(4); N1−Co1−N2, 88.0(2); N1−Co1−N4, 92.7(2); N1−Co1−N5, 173.9(2); N1−Co1−O1, 91.5(2); N1−Co1−O2, 90.9(2); N2−Co1−N4, 93.4(2); N2−Co1−N5, 89.8(2); N2−Co1−O1, 177.3(2); N2−Co1−O2, 90.5(2); N4−Co1−N5, 81.7(2); N4−Co1−O1, 89.3(2); N4−Co1−O2, 174.8(2); N5−Co1−O1, 90.9(2); N5−Co1−O2, 94.9(2); O1−Co1−O2, 86.9(2).

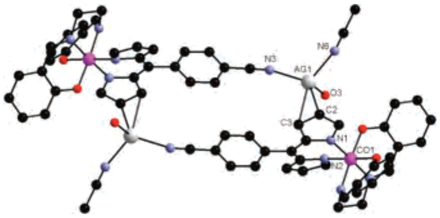

Figure 4. View of the $[(\mathbf{5})Ag(NCCH_3)(H_2O)]_2^{2+}$ metallamacrocycle. SbF_6^- anions and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C2−C3, 1.401(6); Ag1−C2, 2.449(4); Ag1−C3, 2.614(4); Ag1−N3, 2.270(4); Ag1−N6, 2.245(4); Ag1−O3, 2.423(3); Co1−N1, 1.923(3); Co1−N2, 1.940(3); N3−Ag1−N6, 113.02(15); N3−Ag1−O3, 115.92(13); N3−Ag1−C2, 116.90(14); N3−Ag1−C3, 93.39(14); N6−Ag1−O3, 93.38(13); N6−Ag1−C2, 110.43(15); N6−Ag1−C3, 142.31(15); O3−Ag1−C2, 104.53(12); O3−Ag1−C3, 98.75(11); C2−Ag1−C3, 31.92(14).

[*N*,*N′*-bis(salicylidene)ethylenediamine] is an interesting ligand for the formation of heteroleptic complexes because, although this ligand usually coordinates in a square-planar fashion, it may also adopt a twisted conformation when combined with metal centers chelated by an additional bidentate ligand.[15] The reaction of $(salen)Co^{II}\cdot H_2O$ with 1 equiv of **1** afforded, in 27% yield after purification, the complex $(salen)Co^{III}(\mathbf{1})$, compound **5**, the first heteroleptic cobalt complex incorporating the dpm core structurally characterized. Note that several other heteroleptic complexes have been reported.[5f−h,12,16] The loss of symmetry of the salen ligand is apparent in the NMR spectrum of **5**[10c] and is confirmed by single-crystal X-ray diffraction analysis.[11c] The crystal (orthorhombic, $Pna2_1$), a chloroform solvate, is composed of the complex **5** and two $CHCl_3$ molecules in general positions. In this complex (Figure 3), the Co^{III} center adopts the octahedral coordination geometry and is surrounded by the salen and the deprotonated dpm **3** as dianionic tetradentate and monoanionic chelate-type ligands, respectively. The salen moiety adopts a twisted conformation. The $Co-N_{dpm}$ bond distances are similar to those reported for homoleptic $Co(dpm)_3$ complexes.[3,5c,i] However, unlike the latter complexes, the two pyrrolic rings are not coplanar but form a dihedral angle of 24.1°.

Complex **5** possesses a benzonitrile moiety at its periphery. Although for **5** the coordination geometry around Co^{III} is octahedral, it may be compared to the (hfac)Cu(**3**) complex (hfac = hexafluoroacetylacetonate), which also offers such a coordinating site. In the presence of silver salts, (hfac)-Cu(**3**) leads to Ag−π-type interactions.[6] On the other hand, the $Co(\mathbf{3})_3$ complex possessing three free nitrile groups leads to the formation of a 3-D coordination network via only silver−nitrile interactions.[3b] It appeared interesting to further investigate the coordination ability of the complex **5** toward Ag^+ cations. Upon slow evaporation of a stoichiometric mixture of **5** and $Ag(SbF_6)$ in benzene/MeCN, dark-red crystals have been obtained after ca. 7 days.[10d] Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with one complex **5**, one Ag^+ cation, one SbF_6^- anion, one H_2O molecule, and one CH_3CN molecule in general positions.[11d] Interestingly, as shown in Figure 4, two complexes **5** and two Ag^+ cations form a heteronuclear metallamacrocycle. In marked contrast with the metallamacrocycle **4** obtained by combining **1** with Ag^+, in the present case, because both N atoms of the dpm moiety are engaged in the binding of the Co center, the Ag^+ cation, in addition to being coordinated to the nitrile group of **5**, a H_2O molecule, and a MeCN molecule, interacts with one C═C bond of the pyrrole ring (C2−C3) belonging to the neighboring complex. The Ag−C distances as well as the distance of the Ag atom from the mean plane of the pyrrole ring (2.40 Å) are consistent with a Ag−π interaction.[13] This observation correlates well with our previous report on Ag^+−C═C interaction recently described for other systems based on $Zn(dpm)_2/Ag(OTf)$ and $Cu(dpm)_2/Ag(OTf)$.[6] It is worth emphasizing that so far the $Ag-C_{pyrrole}$ interaction had been observed in the solid state only with triflate salts, a slightly coordinating anion, and either square-planar or tetrahedral dpm−metal complexes. The present result shows clearly that this type of interaction seems rather general and may be also obtained with noncoordinating anions such as SbF_6^- and for complexes with octahedral coordination geometry such as a Co^{III} complex.

In conclusion, we have demonstrated that compound **1** may be used to generate a hydrogen-bonded network in its protonated state and a homonuclear metallamacrocycle with Ag^+ cations in its neutral form. For its deprotonated state, **1** acts as a chelate for Co and forms a Ag−π interaction, leading to a heteronuclear metallamacrocycle.

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Supporting Information Available: X-ray crystallographic data for compounds **2** and **4**−**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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