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Supramolecular Chemistry and Anion Binding in Palladium(II) and Silver(I) Complexes Containing *N*,*N*′-Dipyridylxanthene-4,5-dicarboxamide Ligands

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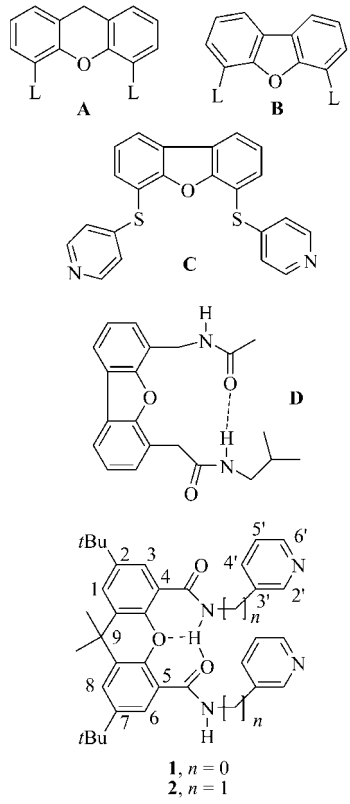
Two new ligands, 2,7-di-*tert*-butyl-9,9-dimethyl-*N*,*N*′-di(3-pyridyl)- (**1**) and -*N*,*N*′-bis[(3-pyridyl)methyl]xanthene-4,5-dicarboxamide (**2**), and their complexes with palladium(II) and silver(I) are reported. Intramolecular hydrogen bonding orients the ligands so as to favour formation of macrocyclic complexes, and the structures of $[Pd_2X_4(\mu\text{-}\mathbf{1})_2]$ (**3a**), X = Cl; (**3b**) X = Br, and $[Ag_2(\mu\text{-}\mathbf{2})_2](CF_3SO_3)_2$ (**5a**) are reported. Intermolecular hydrogen bonding can also occur and can lead to supramolecular self-assembly to give sheet **3a** or ribbon **5a** structures, or serve to bind anions or solvent molecules.

Introduction

In the field of host–guest chemistry, there is increasing interest in the use of hybrid organic–inorganic receptors, which can be synthesized easily by the techniques of self-assembly, and in which both the organic and inorganic components can have useful functions in binding different types of guest molecules or ions.[1–5] If the organic component contains hydrogen-bonding functionality, such as an amide group, this can be used to control the ligand conformation through intraligand hydrogen bonding, and hence to determine the primary structure of the complex (for example, chelate complex, macrocycle or polymer).[6,7] In addition, the hydrogen-bonding component may control secondary or tertiary structure through further interligand hydrogen bonding, and it may be used to enhance host–guest interactions.[1–15] Thus, the combination of dynamic coordination chemistry and hydrogen bonding has proved to be particularly useful for the self-assembly of functional molecular materials.

Ligands based on the xanthene or dibenzofuran skeletons have been widely used in catalysis, because the wide bite angles that are typical with ligands of type **A** or **B** (Scheme 1) can lead to unusual reactivity.[16–23] However, they have been used less frequently in studies of self-assembly or host–guest chemistry,[24–26] though interesting ligands such as **C** (Scheme 1) have been designed.[25] In addition, xanthene skeletons with additional amide functions incorporated, such as **D** (Scheme 1), have been used as mimics for β turns in protein analogs, using intramolecular hydrogen bonds to control the β-turn orientation.[27,28] Following our interest in the self-assembly of host molecules,[29–38] this article reports silver(I) and palladium(II) complexes derived from the *N*,*N*′-di(3-pyridyl)- or *N*,*N*′-bis[(3-pyridyl)methyl]xanthene-4,5-dicarboxamide ligands **1** and **2** (Scheme 1). The ligand is designed to give easy self-



Scheme 1. The *N*,*N*′-dipyridyl-substituted xanthenedicarboxamide ligands **1** and **2**, and some related compounds containing the xanthene or dibenzofuran scaffold unit. The labelling system is defined for ligands **1** and **2**.

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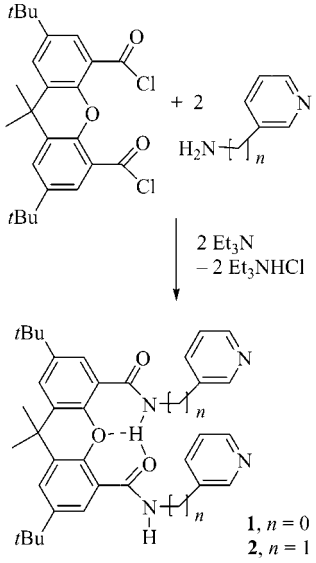
assembly of metallacyclic complexes by dynamic coordination using the pyridine groups as donors. In addition, the amide groups can be used both to orient the donor groups through intramolecular NH···O=C hydrogen bonding and to control either intermolecular assembly or host-guest chemistry through the second NH, C=O group functionality.[27–38]

Results and Discussion

Properties of the Ligands 1 and 2

The ligands were prepared according to Equation (1).



(1)

The ligand **2** was sufficiently soluble in CD_2Cl_2 to allow a study by variable-temperature NMR (Figure 1). It has previously been shown that in xanthenecarboxamide derivatives hydrogen-bonded NH proton signals appear in the region δ = 7–9 ppm and exhibit a large temperature dependence [$\Delta\delta/\Delta T < -10$ ppb/K], while free N–*H* signals appear at $\delta \approx 6$ ppm and exhibit a small temperature dependence [$\Delta\delta/\Delta T \approx -1$ ppb/K].[27,28] The resonance for the NH protons of ligand **2** occurs at δ = 8.18 ppm at 299 K and gives a value of $\Delta\delta/\Delta T = -12$ ppb/K. Only a single set of aromatic resonances was observed, indicating effective twofold symmetry (Figure 1). These data indicate that there is an easy equilibrium between the conformers **2a**, **2b** and **2c** in solution, with the equilibrium favoring the hydrogen-bonded forms (Scheme 2). The ligand **1** was insufficiently soluble in CD_2Cl_2 to allow a similar NMR study, but it is likely that a similar equilibrium is present. In the ^{1}H NMR spectrum of **1** in CD_2Cl_2/CD_3OD, the NH proton exchanged rapidly with the methanol proton and so was not observed.

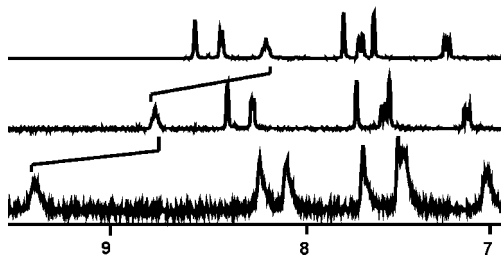
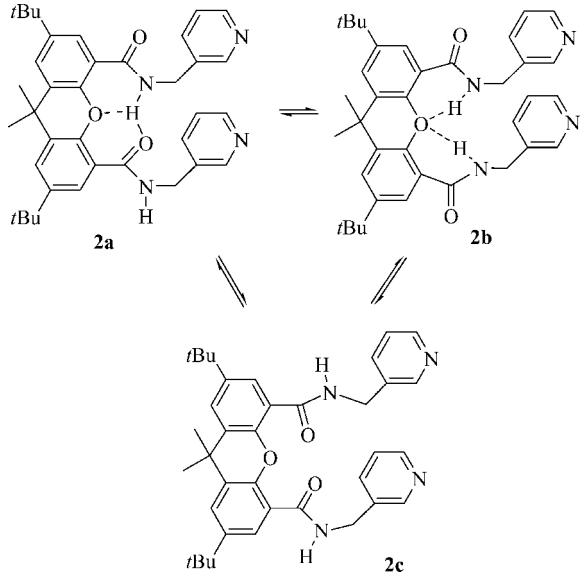


Figure 1. Variable-temperature ^{1}H NMR spectra (400 MHz, top, 299 K; center, 233 K; bottom, 193 K) of ligand **2** in CD_2Cl_2. The bars indicate the movement of the resonance for the NH protons.

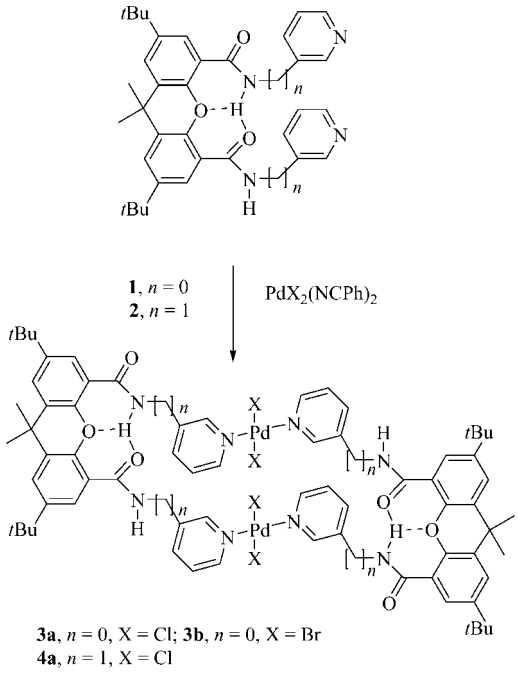


Scheme 2. Probable conformers of ligand **2** arising from rotation of the amide groups.

Palladium(II) Complexes

Reaction of equimolar amounts of ligand **1** and $[PdX_2(NCPh)_2]$ gave the corresponding macrocyclic complexes $[Pd_2X_4(\mu\text{-}\mathbf{1})_2]$ (**3a**), X = Cl; (**3b**), X = Br (Scheme 3). Complex **3a** was essentially insoluble in common organic solvents, but **3b** was sufficiently soluble in [D_7]DMF to give a ^{1}H NMR spectrum. The spectrum indicated effective twofold symmetry, because only a single set of resonances for the ligand **1** was observed. The amide NH resonance for **3b** was observed at δ = 10.75 ppm.

Single crystals of **3a** and **3b** were grown by slow diffusion of a solution of ligand **1** in acetonitrile/methanol into a solution of $[PdX_2(NCPh)_2]$, X = Cl or Br, in dichloromethane, under which conditions each complex crystallized as the acetonitrile solvate $[Pd_2X_4(\mu\text{-}\mathbf{1})_2]\cdot 4MeCN$. The molecular structures are shown in Figure 2. The complexes exist as macrocycles, with each palladium(II) center having the *trans*-$PdCl_2N_2$ square-planar coordination. There is a crystallographically imposed inversion center in both **3a** and **3b** (Figure 2). All amide groups are in the usual *trans* conformation. Each ligand has one NH and one C=O group directed inwards, with a transannular NH···O=C hydrogen bond between them, and one NH and C=O group directed



Scheme 3. Synthesis of macrocyclic palladium(II) complexes.

outwards. The inward NH group is also hydrogen-bonded to the xanthene oxygen atom (Figure 2). In complex **3b**, the outward NH group is hydrogen-bonded to an acetonitrile solvate molecule (Figure 2), but in **3a** the hydrogen bonding of the outward NH group is more complex, as described below. The other main difference in molecular structures of **3a** and **3b** is related to the conformations of the 3-pyridyl groups. In complex **3a** both pyridyl donors are roughly *syn* to the amide carbonyl group [dihedral angles C(8)N(7)C(3)C(2) –19.7°, C(34)N(36)C(37)C(38) –19.8°], but in complex **3b** one of the pyridyl groups is roughly *syn* and the other roughly *anti* to the amide carbonyl group [dihedral angles C(8)N(7)C(3)C(2) –34.7°, C(34)N(36)C(37)C(38) –136.9°]. The above torsion angles and the illustrations in Figure 2 also illustrate how the 3-pyridyl groups are distorted out of the plane of the amide units to a greater extent in **3b** compared to **3a**. As a result of the conformational difference, the palladium atoms are closer and the macrocycle more rectangular in shape in **3b** compared to **3a** [Pd···PdA 5.67 Å in **3a**; Pd···PdA 4.26 Å in **3b**].

In complex **3a** the acetonitrile molecules of solvation are not involved in hydrogen bonding with the outward NH group. Instead this NH group forms an intermolecular hydrogen bond to a chloride ligand of a neighboring molecule (Figure 3a). Each macrocycle **3a** is involved in four such hydrogen-bonding interactions through the two outward-directed NH groups and two of the four chloride ligands (Figure 3b). The overall result is that the macrocycles are assembled into sheets as shown in part b of Figure 3. This intermolecular hydrogen bonding is evidently strong enough to make complex **3a** much less soluble than **3b**. The outward-directed carbonyl group is not involved in hydrogen bonding in either complex **3a** or **3b**, and so it appears that the strength of intermolecular hydrogen bonding of the

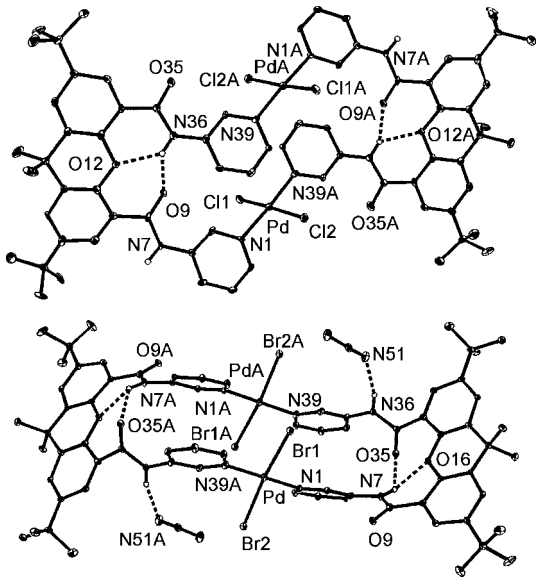


Figure 2. Molecular structures of complexes **3a** and **3b**. Selected distances: **3a**; Pd–Cl(1) 2.320(2); Pd–Cl(2) 2.293(2); Pd–N(1) 2.040(6); Pd–N(39A) 1.997(6) Å. **3b**; Pd–N(1) 1.999(7); Pd–N(39A) 2.016(7); Pd–Br(2) 2.419(1); Pd–Br(1) 2.442(1) Å. Hydrogen bond lengths: **3a**; N(36)···O(12) 2.706(8); N(36)···O(9) 2.843(7) Å. **3b**; N(7)···O(16) 2.641; N(7)···O(35) 3.081; N(36)···N(51) 3.02(1) Å.

outward NH group follows the series NH···ClPd (observed in **3a**) > NH···NCMe (observed in **3b**) > NH···BrPd, NH···O=C (not observed).

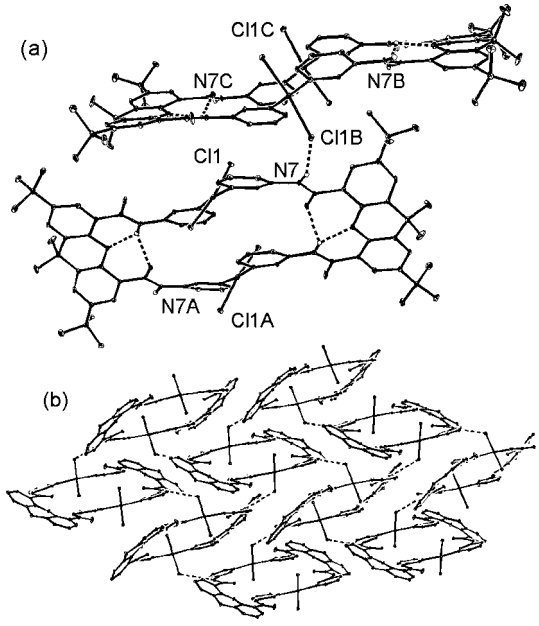
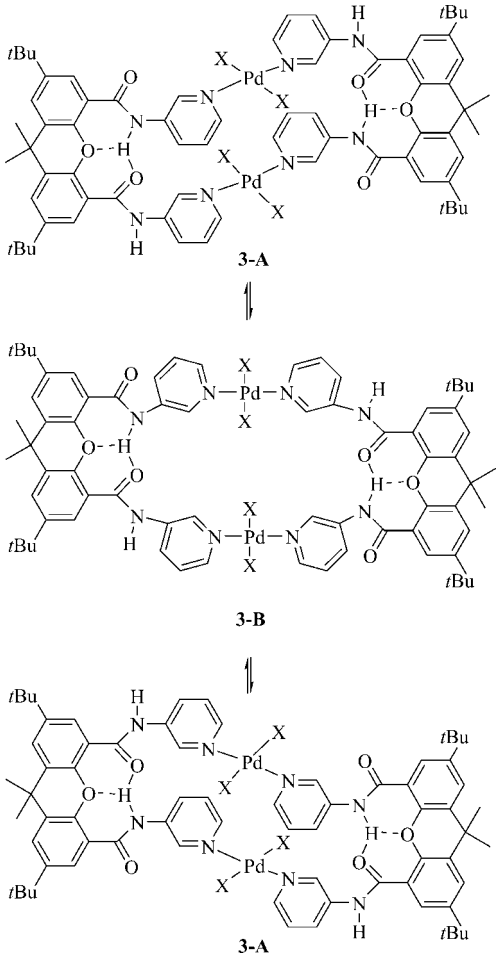


Figure 3. The self-assembly of the macrocyclic complexes **3a**: (a) an intermolecular NH···Cl interaction with distance N(7)···Cl(1B) 3.585(7) Å; (b) the sheet structure arising from the self-assembly process.

The apparent twofold symmetry of complex **3b** in solution, as determined by its ^{1}H NMR spectrum, requires easy rotation of the pyridylamido units and it is likely that the

conformers **3-A** (as seen in the solid-state structure of **3a**) and **3-B** (as seen in **3b**) are two of several that may be involved in the fluxionality (Scheme 4).



Scheme 4. Proposed mechanism of fluxionality of complex **3b** (X = Br).

The reaction of ligand **2** with $[PdCl_2(NCPh)_2]$ was more complex. The product analysed as "$PdCl_2$(**2**)", but the ^{1}H NMR spectrum indicated the presence of two isomers in a roughly 3:2 ratio, each having twofold symmetry (see Exp. Sect.). Single crystals for X-ray structure determination could not be obtained. The ESI-MS gave the highest mass peak envelope centered at *m*/*z* = 1499, corresponding to $[Pd_2Cl_3(\mu\text{-}\mathbf{2})_2]^+$, as expected for loss of one chloride ligand from **4a**. Hence, it is likely that one of the isomers present is **4a** but the nature of the other isomer is not known.

Silver(I) Complexes

The reactions of ligand **1** with silver(I) salts gave insoluble complexes which could not be characterized, but the similar reaction with the more flexible ligand **2** gave the more soluble complexes $[Ag_2(\mu\text{-}\mathbf{2})]_2(X)_2$, **5a**, X = CF_3SO_3; **5b**, X = CF_3CO_2; **5c**, X = NO_3; **5d**, X = BF_4; **5e**, X = PF_6. Complex **5a** was not easily soluble in dichloromethane but it was sufficiently soluble in a CD_2Cl_2/CD_3OD mixture to give a ^{1}H NMR spectrum. The ^{1}H NMR spectrum in the temperature range 299–193 K indicated effective twofold symmetry of the ligand units **2**, presumably due to easy rotation of the pyridylamido units. In contrast to the case of complex **4a**, only one isomer was present (Figure 4). The resonance for the NH protons of complex **5a** occurs at δ = 9.17 ppm at 299 K and gives a value of $\Delta\delta/\Delta T$ = –3 ppb/K.

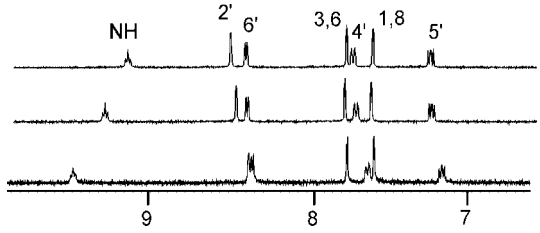


Figure 4. ^{1}H NMR spectrum (400 MHz) of complex **5a** in CD_2Cl_2/CD_3OD at (top) 299 K; (center) 273 K; (bottom) 243 K.

The structure of complex **5a** is shown in Figure 5. The complex exists in the form of a macrocycle with distorted linear silver(I) coordination [N(1)–Ag–N(41A) 168.9(3)°]. The distortion from linearity allows the silver(I) centers to form a transannular argentophilic interaction [Ag–Ag(A) 3.134(1) Å]. The conformation of the amido groups is similar to those observed in **3a** and **3b**, in which the inward NH group hydrogen bonds to both the xanthene oxygen atom and the inward directed carbonyl oxygen atom (Figure 5). The outward directed NH groups hydrogen bond to triflate anions.

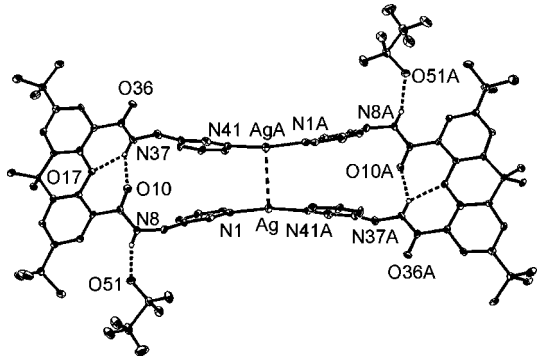


Figure 5. Structure of the silver(I) complex **5a**. Selected parameters: Ag–N(1) 2.130(7), Ag–N(41A) 2.148(7), Ag–Ag(A) 3.134(1) Å; N(1)–Ag–N(41A) 168.9(3)°. Hydrogen bonding distances: N(8)···O(51) 2.92(1), N(37)···O(10) 2.83(1), N(37)···O(17) 2.71(1) Å.

The complex **5a** undergoes further self-assembly in the solid state to give a ribbon structure, as shown in Figure 6. Each triflate ion is hydrogen-bonded to an outward-directed NH group through one of its oxygen atoms (O51), as shown in Figure 5, but each triflate also bridges between the two silver(I) centers of a neighboring macrocycle through a second oxygen atom (O52), as shown in Figure 6. Each macrocycle then interacts with four bridging triflate ions through secondary Ag···O or NH···O interactions, as shown in Figure 6, and a ribbon structure is formed.

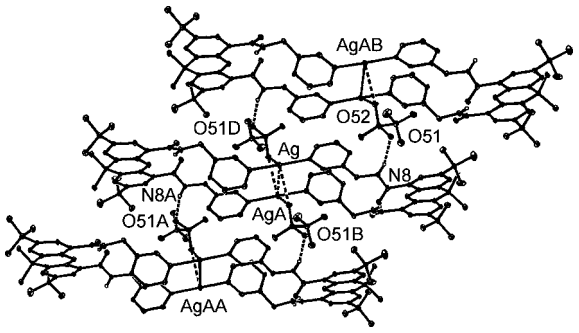


Figure 6. The ribbon structure formed by self-assembly of **5a**, showing how each macrocycle binds to two neighboring macrocycles through four bridging triflate ions. Selected distances: Ag···O(52B) and AgA···O(52D) 2.77(1), Ag···O(52D) and AgA···O(52B) 2.83(1) Å.

The interactions of complexes **5a**–**5e** with anions in dilute acetonitrile solution were studied by ESI-MS. The highest mass peaks for complexes **5a**–**5e** were observed in envelopes centered at *m*/*z* = 1546, 1511, 1458, 1483, and 1541, corresponding to $[^{107}Ag_2(\mathbf{2})_2X]^+$, with X = O_3SCF_3, O_2CCF_3, NO_3, BF_4, and PF_6, respectively. A dilute solution of complex **5a** (0.5×10^{-3} M) in acetonitrile was treated with increasing amounts of $Bu_4N^+X^-$ (X = NO_3, HSO_4, ClO_4, BF_4 and PF_6) to give 1:0.6, 1:0.8, 1:1.0, 1:1.2 and 1:1.4 molar ratios. By monitoring the decrease in intensity of the envelope of peaks for $[Ag_2(\mathbf{2})_2(O_3SCF_3)]^+$ at *m*/*z* = 1545, accompanied by the increase in intensity of the peaks for $[Ag_2(\mathbf{2})_2X]^+$, it is possible to estimate the relative binding abilities of the anions X^-. Typical spectra are shown in Figure 7. The anion binding follows the sequence $NO_3^- > HSO_4^- > CF_3SO_3^- > ClO_4^- > BF_4^-, PF_6^-$. This is consistent either with the series of pK_a values of the corresponding acids [approximate pK_a for HNO_3 –1; H_2SO_4 –3; $HClO_4$ –10; CF_3SO_3H –13] or with the coordinating ability of the anions.[39] Hence it is not obvious if the anions mainly associate with the cation $[Ag_2(\mu\text{-}\mathbf{2})_2]^{2+}$ primarily by coordination to silver(I) or by hydrogen bonding to one of the outward-directed NH groups.

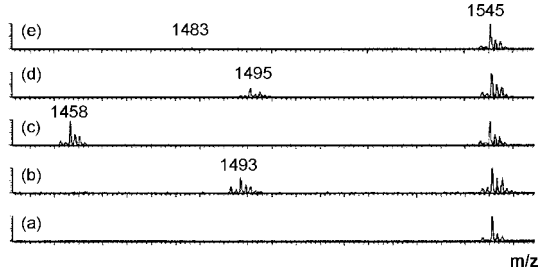


Figure 7. ESI-MS for complex **5a** in acetonitrile either alone (a) or in the presence of 1.4 equiv. of Bu_4NX: (b) X = HSO_4; (c) X = NO_3; (d) X = ClO_4; (e) X = BF_4.

Conclusions

The intramolecular hydrogen bonding observed for ligands **1** and **2** serves to favor a U-shaped molecule [Scheme 1, Equation (1)] and this in turn favors formation of macrocyclic complexes with palladium(II) and silver(I). In the case of the ligand **1** only macrocyclic complexes **3a** and **3b** are formed with palladium(II) halides (Scheme 3, Figure 2) but, in the case of the more flexible ligand **2** a second isomer is formed. Examination by molecular mechanics indicates that either a monomer with chelating ligand **2** or a *cis*,*cis* dimer with bridging ligands **2** are possible for this second isomer. With silver(I), the ligand **2** forms a macrocyclic complex $[Ag_2(\mu\text{-}\mathbf{2})_2]^{2+}$ and, in the triflate salt, the anions form secondary bonds to both silver(I) and to an NH group of the ligand.

An interesting feature of the macrocyclic complexes is that there are two outward-directed NH groups available to take part in hydrogen bonding (Scheme 2). In the palladium(II) complexes **3a** and **3b**, these NH groups form hydrogen bonds to either solvent molecules (**3b**) or to chloride ligands of neighboring macrocycles (**3a**) (Figure 2 and Figure 3). In complex **3a**, this intermolecular hydrogen bonding leads to supramolecular self-assembly of a sheet structure (Figure 3). In the silver(I) complex **5a**, the outward-directed NH groups form hydrogen bonds to triflate anions (Figure 5). The triflate anions then use a second oxygen atom to form a weak coordinate bond to the two silver(I) centers of a neighboring macrocycle. The overall result is then the formation of a supramolecular "ribbon of macrocycles" structure (Figure 6). The ESI-MS of **5a** in acetonitrile solution indicates that at least partial association between the cations $[Ag_2(\mu\text{-}\mathbf{2})_2]^{2+}$ and triflate anions occurs giving the major ion $[Ag_2(\mu\text{-}\mathbf{2})_2(CF_3SO_3)]^+$. As expected, anion exchange occurs easily with other anions X^- such as HSO_4^-, NO_3^-, ClO_4^-, BF_4^- and PF_6^- to give the corresponding ions $[Ag_2(\mu\text{-}\mathbf{2})_2(X)]^+$ (Figure 7). In all of the complexes, there is easy exchange in solution between the inward and outward directed NH groups, and this occurs by easy rotation of the 3-pyridylamide units (Scheme 4).

Overall, this first study of coordination complexes of ligands with amide group substituents on the xanthene scaffold indicates the promise that exists for both supramolecular self-assembly and host-guest chemistry through various forms of hydrogen bonding with the outward-directed NH groups.

Experimental Section

NMR spectra were recorded with a Varian Inova 400 MHz spectrometer. For atom labeling see Scheme 1.

2,7-Di-*tert*-butyl-9,9-dimethyl-*N*,*N*′-di(3-pyridyl)xanthene-4,5-dicarboxamide (1): A solution of 3-aminopyridine (0.21 g, 2.23 mmol) in dichloromethane (20 mL) was added to a solution of 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4,5-dicarbonyl dichloride (0.50 g, 1.12 mmol) and triethylamine (0.34 g, 3.35 mmol) in dry dichloromethane (50 mL). The reaction mixture was stirred overnight under nitrogen, then the solvent was evaporated under vacuum, and the residue was washed with water and acetone to give the product as a white solid. Yield: 0.33 g (52%). ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 8.59 (s, 2 H, 2′-H), 8.19 (d, J_{HH} = 5 Hz, 2 H, 6′-H), 7.98 (d, J_{HH} = 7 Hz, 2 H, 4′-H), 7.78 (s, 2 H, 3-H, 6-H), 7.66 (s, 2 H, 1-H, 8-

H), 7.11 (dd, J_{HH} = 5 Hz, 7 Hz, 2 H, 5′-H), 1.70 (s, 6 H, CH_3), 1.36 (s, 18 H, *t*Bu) ppm. $C_{35}H_{38}N_4O_3$ (562.71): calcd. C 74.71, H 6.81, N 9.96; found C 74.41, H 6.42, N 10.44.

2,7-Di-*tert*-butyl-9,9-dimethyl-*N*,*N*′-bis[(3-pyridyl)methyl]xanthene-4,5-dicarboxamide (2): This compound was prepared according to the procedure described above for **1**. 3-(Aminomethyl)pyridine was used instead of 3-aminopyridine. Yield: 35%. ^{1}H NMR (CD_2Cl_2): δ = 8.57 (s, 2 H, 2′-H), 8.44 (d, J_{HH} = 5 Hz, 2 H, 6′-H), 8.19 (t, J_{HH} = 5 Hz, 2 H, CONH), 7.77 (s, 2 H, 3-H, 6-H), 7.69 (d, J_{HH} = 8 Hz, 2 H, 4′-H), 7.60 (s, 2 H, 1-H, 8-H), 7.21 (dd, J_{HH} = 5 Hz, 8 Hz, 2 H, 5′-H), 4.51 (d, J_{HH} = 5 Hz, 4 H, CH_2), 1.68 (s, 6 H, CH_3), 1.33 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 167.6 (C=O), 148.9, 148.3, 146.8, 146.2, 136.5, 135.9, 130.6, 127.0, 126.1, 124.4, 121.7, 41.52 (CH_2), 35.1 (CH_3), 33.0 (CH_3), 51.5 (*t*Bu) ppm. $C_{37}H_{42}N_4O_3$ (590.76): calcd. C 75.23, H 7.17, N 9.48; found C 75.28, H 7.20, N 9.09.

[Pd$_2$Cl$_4$(μ-1)$_2$] (3a): A solution of the ligand **1** (0.0154 g, 0.026 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [$PdCl_2$(NCPh)$_2$] (0.010 g, 0.026 mmol) in CH_2Cl_2 (10 mL) was added. The solution was stirred overnight, then pentane (40 mL) was added, and the yellow solid product which precipitated was collected by filtration and dried under vacuum. Yield: 0.013 g. The product was insufficiently soluble to give an NMR spectrum. $C_{70}H_{76}Cl_4N_8O_6Pd_2$ (1480.03): calcd. C 56.81, H 5.18, N 7.57; found C 56.64, H 5.00, N 7.47.

[Pd$_2$Br$_4$(μ-1)$_2$] (3b): A solution of the ligand **1** (0.036 g; 0.064 mmol) in dichloromethane (10 mL) was added to a solution [$PdBr_2$(NCPh)$_2$] (0.030 g, 0.064 mmol) in a mixture of acetonitrile (5 mL) and dichloromethane (5 mL). The solution was stirred overnight, then pentane (40 mL) was added, and the yellow solid product was collected by filtration and dried under vacuum. Yield: 0.043 g. ^{1}H NMR ([D$_7$]DMF): δ = 10.75 (s, 4 H, CONH), 9.30 (s, 4 H, -2′-H), 8.82 (d, J_{HH} = 6 Hz, 4 H, 6′-H), 8.04 (d, J_{HH} = 8 Hz, 4′-H), 7.84 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.69 (d, J_{HH} = 2 Hz, 4 H, 1-H, 8-H), 7.18 (dd, J_{HH} = 6 Hz, 8 Hz, 4 H, 5′-H), 1.77 (br. s, 12 H, CH_3), 1.38 (br. s, 36 H, *t*Bu) ppm. $C_{70}H_{76}Br_4N_8O_6Pd_2 \cdot H_2O$ (1657.84): calcd. C 50.17, H 4.69, N 6.69; found C 50.40, H 4.54, N 6.45.

[Pd$_2$Cl$_4$(μ-2)$_2$] (4): A solution of the ligand **2** (0.0154 g; 0.026 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [$PdCl_2$(NCPh)$_2$] (0.010 g; 0.026 mmol) in CH_2Cl_2 (10 mL). The solution was stirred overnight and the product was isolated as above. Yield: 0.013 g. ^{1}H NMR (CD_2Cl_2/CD_3OD), isomer (**a**): δ = 9.15 (s, 2 H, 2′-H), 8.80 (d, J_{HH} = 6 Hz, 2 H, 6′-H), 8.20 (br. t, 2 H, CONH), 7.68 (d, J_{HH} = 8 Hz, 2 H, 4′-H), 7.65 (s, 2 H, 3-H, 6-H), 7.56 (s, 2 H, 1-H, 8-H), 7.16 (dd, J_{HH} = 8 Hz, 6 Hz, 2 H, 5′-H), 4.36 (s, 4 H, CH_2), 1.66 (s, 6 H, CH_3), 1.33 (s, 18 H, *t*Bu) ppm. Isomer (**b**): δ = 9.20 (s, 2 H, 2′-H), 8.70 (d, J_{HH} = 6 Hz, 2 H, 6′-H), 8.45 (br. t, 2 H, CONH), 7.88 (d, J_{HH} = 8 Hz, 2 H, 4′-H), 7.67 (s, 2 H, 3-H, 6-H), 7.59 (s, 2 H, 1-H, 8-H), 7.48 (dd, J_{HH} = 8 Hz, 6 Hz, 2 H, 5′-H), 4.23 (s, 4 H, CH_2), 1.64 (s, 6 H, CH_3), 1.30 (s, 18 H, *t*Bu) ppm. $C_{74}H_{87}Cl_4N_8O_6Pd_2$ (1539.16): calcd. C 57.86, H 5.51, N 7.29; found C 57.84, H 5.85, N 7.32.

[Ag$_2$(μ-2)$_2$][CF$_3$SO$_3$]$_2$ (5a): A solution of the ligand **2** (0.046 g, 0.078 mmol) in THF (10 mL) was added to a solution of AgO_3SCF_3 (0.020 g, 0.078 mmol) in acetone (10 mL). The solution was stirred overnight. The solvent was evaporated to give a white solid, which was washed with hexane and dried under vacuum. Yield: 0.055 g. ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 9.17 (t, J_{HH} = 6 Hz, 4 H, CONH), 8.53 (s, 4 H, 2′-H), 8.44 (d, J_{HH} = 5 Hz, 4 H, 6′-H), 7.81 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.76 (d, J_{HH} = 8 Hz, 4 H, 4′-H), 7.63 (d, J_{HH} = 2 Hz, 4 H, 1-H, 8-H), 7.37 (dd, J_{HH} = 5 Hz, 8 Hz, 4 H, 5′-H), 4.53 (d, J_{HH} = 6 Hz, 8 H, CH_2), 1.66 (s, 12 H, CH_3), 1.33 (s, 36 H, *t*Bu) ppm. $C_{76}H_{84}Ag_2F_6N_8O_{12}S_2 \cdot H_2O \cdot$THF: calcd. C 53.81, H 5.31, N 6.28; found C 53.85, H 5.17, N 6.08. Colourless plate crystals of **5a**·4$CHCl_3$ were obtained by slow diffusion of a concentrated solution of ligand **2** in chloroform into a concentrated solution of [AgO_3SCF_3] in acetone.

Similarly were prepared: **[Ag$_2$(μ-2)$_2$][CF$_3$CO$_2$]$_2$ (5b):** Yield: 34%. ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 9.02 (br. t, 4 H, CONH), 8.47 (br. s, 4 H, 2′-H), 8.38 (d, J_{HH} = 6 Hz, 4 H, 6′-H), 7.80 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.78 (br. m, 4 H, 4′-H), 7.62 (d, J_{HH} = 3 Hz, 4 H, 1-H, 8-H), 7.27 (br. dd, J_{HH} = 6 Hz, 8 Hz, 4 H, 5′-H), 4.53 (br. d, J_{HH} = 4 Hz, 8 H, CH_2), 1.66 (s, 12 H, CH_3), 1.33 (s, 36 H, *t*Bu) ppm. $C_{78}H_{84}Ag_2F_6N_8O_{10} \cdot 2CH_2Cl_2 \cdot 2H_2O \cdot 2(CH_3)_2CO \cdot C_5H_{12}$ (1623.29): calcd. C 54.18, H 5.80, N 5.55; found C 54.39, H 4.95, N 5.64. **[Ag$_2$(μ-2)$_2$][NO$_3$]$_2$ (5c):** Yield: 84%. ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 9.23 (br. t, J_{HH} = 6 Hz, 4 H, CONH), 8.52 (br. s, 4 H, 2′-H), 8.42 (d, J_{HH} = 5 Hz, 4 H, 6′-H), 7.82 (br. d, J_{HH} = 8 Hz, 4 H, 4′-H), 7.81 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.64 (d, J_{HH} = 3 Hz, 4 H, 1-H, 8-H), 7.34 (dd, J_{HH} = 5 Hz, 8 Hz, 4 H, 5′-H), 4.48 (br. d, J_{HH} = 4 Hz, 8 H, CH_2), 1.67 (s, 12 H, CH_3), 1.33 (s, 36 H, *t*Bu) ppm. $C_{76}H_{90}Ag_2N_{10}O_{12} \cdot 6H_2O$: calcd. C 55.01, H 6.20, N 8.44; found C 54.98, H 5.57, N 8.46. **[Ag$_2$(μ-2)$_2$][BF$_4$]$_2$ (5d):** Yield: 62%. ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 9.06 (br. t, J_{HH} = 6 Hz, 4 H, CONH), 8.52 (br. s, 4 H, 2′-H), 8.41 (d, J_{HH} = 5 Hz, 4 H, 6′-H), 7.82 (br. d, J_{HH} = 8 Hz, 4 H, 4′-H), 7.80 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.64 (d, J_{HH} = 2 Hz, 4 H, 1-H, 8-H), 7.33 (br. dd, J_{HH} = 6 Hz, 8 Hz, 4 H, 5′-H), 4.55 (br. d, J_{HH} = 5 Hz, 8 H, CH_2), 1.67 (s, 12 H, CH_3), 1.33 (s, 36 H, *t*Bu) ppm. $C_{94}H_{132}Ag_2B_2Cl_6F_8N_8O_{12} \cdot 4H_2O \cdot (CH_3)_2CO$ (2168.18): calcd. C 54.37, H 5.81, N 6.59; found C 54.33, H 5.59, N 6.49. **[Ag$_2$(μ-2)$_2$][PF$_6$]$_2$ (5e):** Yield: 72%. ^{1}H NMR (CD_2Cl_2/CD_3OD): δ = 9.16 (br. t, J_{HH} = 6 Hz, 4 H, CONH), 8.47 (br. d, J_{HH} = 2 Hz, 4 H, 2′-H), 8.41 (br. d, J_{HH} = 5 Hz, 4 H, 6′-H), 7.86 (br. d, J_{HH} = 8 Hz, 4 H, 4′-H), 7.76 (d, J_{HH} = 2 Hz, 4 H, 3-H, 6-H), 7.63 (d, J_{HH} = 2 Hz, 4 H, 1-H, 8-H), 7.41 (dd, J_{HH} = 5 Hz, 8 Hz, 4 H, 5′-H), 4.54 (br. d, J_{HH} = 6 Hz, 8 H, CH_2), 1.65 (s, 12 H, CH_3), 1.31 (s, 36 H, *t*Bu) ppm. $C_{76}H_{90}Ag_2F_{12}N_8O_6P_2 \cdot H_2O$: calcd. C 52.60, H 5.34, N 6.46; found C 52.74, H 5.51, N 6.12.

ESI-MS: All ESI mass spectra were recorded with a Micromass LCT spectrometer and were calibrated with NaI at a concentration of 2 μg/μL in propan-2-ol/water (50:50). The injection flow rate at 20.0 μL/min was used throughout all experiments. The procedure for anion exchange between **5a** and $Bu_4N^+NO_3^-$ was as follows. A stock solution of $Bu_4N^+NO_3^-$ in acetonitrile (5×10^{-3} M) was used to prepare standard solutions of $Bu_4N^+NO_3^-$ at varying concentrations. To a solution of **5a** in acetonitrile (1 mL, 5×10^{-4} M) was added a solution of $Bu_4N^+NO_3^-$ in acetonitrile (1 mL, 7×10^{-4} M). After 30 min, the ESI-MS was recorded and the ratio of [Ag$_2$(μ-**2**)$_2$(O_3SCF_3)]$^+$ to [Ag$_2$(μ-**2**)$_2$(NO_3)]$^+$ was estimated. The procedure was repeated at several concentrations of $Bu_4N^+NO_3^-$. The same procedure was used to study anion exchange between complex **5a** and $Bu_4N^+X^-$ (X = HSO_4^-, ClO_4^-, BF_4^-, and PF_6^-).

X-ray Structure Determinations: Crystals were mounted on glass fibers, and data were collected at 150 K with a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998). The SHELXTL-NT V6.1 (G. M. Sheldrick, Madison, WI) program package was used to solve and refine the structures by direct methods. The hydrogen atom posi-

Table 1. Crystal data and structure refinement for the complexes.

Complex	**3a**·4MeCN	**3b**·4MeCN	**5a**·2$CHCl_3$
Formula	$C_{78}H_{88}Cl_4N_{12}O_6Pd_2$	$C_{78}H_{88}Br_4N_{12}O_6Pd_2$	$C_{40}H_{44}AgCl_6F_3N_4O_6S$
Fw	1644.20	1822.04	1086.42
T [K]	150(2)	150(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Cell dimensions			
a [Å]	20.643(2)	25.421(2)	13.2529(5)
b [Å]	12.3582(8)	16.839(1)	37.775(1)
c [Å]	16.020(1)	9.3664(6)	9.1803(4)
β [°]	112.822(3)	99.653(3)	94.697(2)
V [Å^3]	3767.0(5)	3952.6(4)	4580.5(3)
Z	2	2	4
$d_{calcd.}$ [Mgm^{-3}]	1.450	1.531	1.575
Absorption coefficient [mm^{-1}]	0.680	2.535	0.897
F(000)	1696	1840	2208
Reflections	22349	29296	36296
Independent reflections	11397	6886	7595
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Data/restraints/parameters	11397/4/471	6886/2/460	7595/0/550
Goof	1.051	0.856	0.882
R_1 [$I > 2\sigma(I)$]	0.077	0.061	0.059
wR_2[$I > 2\sigma(I)$]	0.140	0.092	0.103

tions were calculated geometrically and were included as riding on their respective carbon atoms. Details of the data collection and refinement are given in Table 1. In all three structures, the molecule had a crystallographically imposed center of symmetry.

Orange plate-like crystals of [Pd_2Cl_4(μ-**1**)$_2$]·4MeCN were grown from CH_2Cl_2/MeCN/MeOH. The crystal was twinned and the twin law was determined by using ROTAX, and confirmed by successful refinement. All heavy atoms were refined anisotropically but there were some anomalous thermal parameters and a large R_{int}, associated with imperfect treatment of the crystal twinning and with unresolved disorder of the solvent molecules.

Yellow crystals of [Pd_2Br_4(μ-**1**)$_2$]·4MeCN were grown from CH_2Cl_2/MeCN/MeOH, a concentrated dichloromethane/acetonitrile/methanol solution. One MeCN molecule was well ordered, but the other was not and its geometry was constrained to be the same as the well-ordered one.

Colorless crystals of [Ag_2(μ-**2**)$_2$][CF_3SO_3]$_2$·4$CHCl_3$, were grown from $CHCl_3$/Me_2CO. The refinement was straightforward in this case.

CCDC-632844 to -632846 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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