Synthesis and crystal structures of silver(I) and copper(II) complexes with *p*-xylylene-bridged bipyrazolyl ligands

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Abstract Two semi-rigid bipyrazolyl ligands, namely 2,3,5,6-tetramethyl-1,4-bis[(3',5'-dimethyl-1H -pyrazol-4'yl)methylene]benzene (H₂L) and 2,3,5,6-tetramethyl-1,4bis[(3',5'-diphenyl-1H - pyrazol-4'-yl)methylene]benzene (H_2L') , and their Ag(I) and Cu(II) complexes have been prepared and structurally characterized by means of X-ray analysis. In the structures of the metal complexes, namely $[Ag_2(H_2L)_2](BF_4)_2 \cdot 2H_2O$ (1), $[Ag(H_2L)(NO_3)]_n$ (2), $[Cu_2(H_2L)_4(SO_4)_2] \cdot 11H_2O$ (3), and $\{[Ag(H_2L')]BF_4\}_n$ (4), the bipyrazoles act as bridging ligands to connect two metal atoms. Complexes 2 and 4 exhibit 1-D polymeric structures, while 1 and 3 are discrete molecules with a rectangular dimer or tetragonal prismatic shapes, respectively. Two different conformations, namely cis and trans, have been observed for these bipyrazolyl ligands.

Introduction

Bipyrazoles, in which two pyrazolyl units are linked via covalent bond(s), have recently received much attention [1, 2]. As a type of ligand for metals, they have proven to be more versatile and flexible in construction of metallo-supramolecular assemblies than pyrazole itself. Recent remarkable examples as such include a Cu₆ trigonal prismatic cage [3], a Cu₆ trigonal anti-prismatic cage [4], and a

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series of metallo-macrocycles based on dipalladium corners [5].

We have recently reported the synthesis and crystal structures of a semi-rigid *m*-xylylene-bridged C^4 -linked bipyrazolyl ligand as well as its Ag(I) and Cu(II) complexes [6]. As one might expect, the relative orientations of the two pyrazolyl rings is a key factor to determine the structure of the metal-bipyrazole complexes. Changes in the substituents on the central phenyl ring to which the pyrazolyl units are attached may result in different spatial arrangements of the two pyrazolyl rings and thus different structural motifs upon binding to metals. As one part of our ongoing research on the coordination chemistry of bipyrazoles, we report herein the synthesis and crystal structures of two new p-xylylene-bridged C^4 linked bipyrazolyl ligands (H₂L and H₂L', Scheme 1), in which the pyrazolyl rings are attached to the 1,4-positions of phenyl ring instead of the 1,3-positions as in our previous paper, together with three Ag(I) and one Cu(II) complexes; $[Ag_2(H_2L)_2](BF_4)_2 \cdot 2H_2O$ (1), $[Ag(H_2L)]$ $(NO_3)]_n$ (2), $[Cu_2(H_2L)_4(SO_4)_2] \cdot 11H_2O$ (3), and $\{[Ag(H_2L')]$ BF_4 _n (4). The structural effect of the 3,5-substituents on the conformations of bipyrazole is discussed in this paper.

Results and discussion

Synthesis and characterization

The bipyrazolyl ligands, H_2L and H_2L' , were prepared according to the synthetic route shown in Scheme 1. Both were characterized spectroscopically by IR (Figs. S5, S8) and ¹H NMR (Figs. S6, S9) spectroscopy. It is worth noting that beside the strongest parent ion signal, a second strong

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Scheme 1 Synthetic route for the bipyrazoles (R = Me, H₂L; R = Ph, H₂L')

signal corresponding to a dimeric species is also present in the mass spectrum of H_2L (Fig. S7).

All the metal complexes were prepared in a straightforward way by mixing the appropriate metal salts with bipyrazoles in solution. The three silver complexes were obtained in less than 20% yield; higher concentrations of reactants or faster evaporation/diffusion rates usually resulted in powdery samples instead of crystals. The IR spectra of these complexes show the characteristic peaks of the anions of the metal salts (BF_4^- , SO_4^{2-} , NO_3^-) (Figs. S10, S11, S12, S13); the presence of these anions was later verified by X-ray diffraction analysis.

Crystal structure descriptions

Both bipyrazoles crystallize in space group $P2_1/c$. In their asymmetric units, only half of the molecule is independent, being related to the other half by an inversion center. As depicted in Figs. 1 and 2, in their crystals, both ligands adopt the trans-conformation; the two pyrazolyl groups are located on the opposite sides of the central phenylene ring (Scheme 2). The dihedral angles between pyrazolyl and phenylene rings are 84.5(6) and 86.7(2) for H_2L and H_2L' , respectively. Intramolecular C–H $\cdots\pi$ interactions may exist in H_2L' , as evident by the distance of 2.5293(4) Å from the peripheral phenyl H-atom to the central phenylene ring (Fig. 2). On the other hand, no such interactions can be found for H₂L. This observation implies that H₂L might be more flexible than H₂L', because the absence of the phenyl-phenyl interaction makes the rotation along $C^{4}(pz)$ - $C(-CH_2-)$ or $C(-CH_2-)-C(Ph)$ much easier for the former. In its crystal, molecules of H_2L' are linked into zigzag chains running along the *a*-axis, by pairs of complementary



Fig. 1 Ball-and-stick diagram of the bipyazole H₂L. Except for those bound to N atoms, H atoms are not shown for clarity. Key: N—*dotted ball*, C—*empty ball*, H—*smaller empty ball*

N-H···N hydrogen bonds (N1···N2^{*i*} = 2.907(2) Å, symmetry code: *i*) -x + 1, -y + 1, -z. see Fig. S1).

The complex $[Ag_2(H_2L)_2](BF_4)_2 \cdot 2H_2O$ (1) exhibits a discrete rectangular dimer structure. As shown in Fig. 3, the Ag(I) atom is linear two-coordinate with two cis-arranged pyrazolyl groups belonging to different ligands. Each H₂L ligand, in the *cis*-conformation, acts as a μ_2 bridge binding to two Ag(I) atoms. The dihedral angle between the pyrazolyl and phenylene rings is 83.7(2) for the bipyrazole ligand in **1**. The intramolecular Ag. Ag distance is 3.4412(3) Å, virtually equal to the sum of the van der Waals radii for the Ag atoms (3.44 Å). Furthermore, the face-to-face distance between the two nearly parallel pyrazolyl rings of the adjacent rectangles of 1 is 3.47(1) Å, indicative of $\pi - \pi$ stacking interactions (Fig. S2). With the help of the weak intermolecular interactions of argentophilicity and $\pi - \pi$ stacking, the cations of 1 are joined together to form infinite puckered chains, which are in turn further interconnected via



Fig. 2 Ball-and-stick diagram of H_2L' . Except for the H atoms bound to N atoms and the phenyl H atoms closest to the central phenylene, H atoms are not shown for clarity. The *dashed lines* stand for the C-H $\cdots\pi$ interactions existing in H_2L' . Key: N—*dotted ball*, C—*empty ball*, H—*smaller empty ball*



Scheme 2 Two possible conformations of bipyrazoles H₂L and H₂L'



Fig. 3 Ball-and-stick diagram of the $[Ag_2(H_2L)_2]^{2+}$ cation of complex **1** with atom labels, showing the coordination environment around the Ag atoms and the *cis*-conformation of the μ_2 -bridging ligand. Selected distances (Å) and angles (°): Ag1–N1 = 2.105(3), Ag1–N3a = 2.114(3); N1–Ag1–N3a = 173.76(13). Symmetry codes: (a) -x, -y + 1, -z + 1. Except for the H atoms bound to N atoms, other H atoms are not shown for clarity. Key: N—*dotted ball*, C—*empty ball*, H—*smaller empty ball*, Ag—*cross hatched ball*

 N_{pz} -H···F hydrogen bonds to form planes $(N2\cdots F3^i)$ = 2.809(4) Å, N4···F4ⁱⁱ = 2.953(5) Å. Symmetry codes: (*i*) *x*-1, *y* + 1, *z*; (*ii*) *x* + 1, *y*, *z*. Fig. S3). It is observed that in the crystal structure of **1**, there are channels along the *a*-axis, in which solvent water molecules reside (Fig. S4). A few similar rectangular dimetallomacrocycles based on various metals and ligands are also known in the literature [6, 7].

The complex $\{[Ag(H_2L)](NO_3)\}_n$ (2) exhibits a 1-D chain structure. The Ag(I) atom is linearly coordinated by two *trans*-placed pyrazolyl groups from two adjacent ligands (Fig. 4). The bipyrazole also adopts a *cis*-conformation and acts as a bridge linking two Ag(I) atoms, as in complex 1 (Scheme 2). However, assembly of these units

this time yields 1D structures of M_nL_n type, running along the *c*-axis. The dihedral angle between the pyrazolyl and phenylene rings is 87.9(3)[°] for the bipyrazole ligand in **2**. Interestingly, the shape of the chain looks rather like a "square wave" when viewed down the *b*-axis. It is noteworthy that the structural parameters (e. g. the coordination geometry around metal, bond distances, and angles) of the complex cations in **1** and **2** are very similar, and therefore, they represent an example of supramolecular "ring-opening" isomerism between 0D cyclic M₂L₂ metallacyclic and 1D M_nL_n polymeric motifs [8]. As discussed by Su, some subtle factors such as solvent or anion may play an important role in determining which structural form, among several possible motifs, will be crystallized out from the solution [7].

The complex $[Cu_2(H_2L)_4(SO_4)_2] \cdot 11H_2O(3)$ is a discrete molecular cage. The Cu(II) atom exhibits square pyramidal coordination geometry, with four pyrazolyl N atoms from four bipyrazoles as the base and one O atom of sulfate as the apex. The ligand, again in its cis-conformation, acts as a bridge linking two Cu(II) atoms (Fig. 5). Thus, the connection of four bipyrazoles by two Cu(II) atoms results in a square prismatic cage. The dihedral angle between the pyrazolyl and phenylene rings is 88.7(2) for the ligand in 3. In a recent review, design approaches have been proposed for discrete coordination assemblies based on non-rigid ligands, of which the strategy of "molecular clips + metal ions of C_n symmetry" can be used to predict and explain the structures of the convergent assemblies including M2L2 metallacycles and M₂L₄ tetragonal prisms as reported here and in our previous paper, with the semi-rigid bipyrazoles in cis-conformation acting as "molecular clips" and Ag(I)/ Cu(II) ions as connectors of C_2 or C_4 symmetry, respectively [7].

The complex $\{[Ag(H_2L')](BF_4)\}_n$ (4) exhibits a 1D structure. The Ag(I) atom is linearly two-coordinated by two cis-placed pyrazolyl groups from two adjacent ligands. Unlike the methyl-substituted bipyrazoles in complexes 1, 2, and 3, the phenyl-substituted ligand in complex 4 adopts a trans-conformation and acts as a bridge linking two Ag(I) atoms to form zigzag chains (Scheme 2, Fig. 6). The chain incorporate the N_{pz}-H…F H-bonds, which may further consolidate the infinite structure $(N3 \cdots F3 = 2.764)$ (4) Å, N4…F1 = 2.838(5) Å, N4…F2 = 3.262(5) Å). The face-to-face distance and dihedral angle between the central phenylene ring and the 3(5)-phenyl rings of the same ligand are ca 3.5 Å and $10.6(1)^{\circ}$, $18.7(3)^{\circ}$, $25.1(1)^{\circ}$, $37.34(1)^\circ$, respectively, which indicates the existence of π - π stacking interactions. As shown in Fig. 6, the most prominent feature of this structure is the presence of a triad of stacking phenyl rings. Obviously, this kind of phenylphenyl interaction favors the trans-conformation since the geometry of this ligand does not allow two phenyl



Fig. 4 Ball-and-stick diagram of the $[Ag_n(H_2L)_n]^{n+}$ unit of complex **2** with atom labels, showing the coordination environment around the Ag atoms and the *cis*-conformation of the μ_2 -bridging ligand. Selected distances (Å) and angles (°): Ag1–N1 = 2.132(4), Ag1–



Fig. 5 Ball-and-stick diagram of complex **3**, with atom labels, showing the coordination environment around the Cu atoms and the *cis*-conformation of the μ_2 -bridging ligand. All the methyl groups and H atoms are omitted for clarity. Selected distances (Å) and angles (°): Cu1–N8a = 1.961(5), Cu1–N5 = 1.969(6), Cu1–N3a = 2.023(5), Cu1–N1 = 2.042(5), Cu1–O4 = 2.210(5); N8a–Cu1–N5 = 88.3(2), N8a–Cu1–N3 = 171.00(18), N5–Cu1–N3a = 92.1(2), N8a–Cu1–N1 = 89.2(2), N5–Cu1–N1 = 173.9(2), N3a–Cu1–N1 = 89.5(2), N8a–Cu1–O4 = 95.2(2), N5–Cu1–O4 = 94.7(2), N3a–Cu1–O4 = 93.8(2), N1–Cu1–O4 = 91.0(2). Symmetry codes: a) -x + 1, *y*, -z. Key: N—dotted ball, C—empty ball, Cu—cross hatched ball, S—hatched ball, O—smaller hatched ball

substituents to stack at the same side of the central phenylene ring. It is interesting to note that the phenyl–phenyl interaction shows itself in the form of π – π stacking in 4, instead of the C–H··· π interaction seen in the free ligand. In this sense, the *trans*-conformation observed in complex 4 is actually inherited from the phenyl-substituted bipyrazole and manifests itself rather differently in its Ag(I) complex. Hanton et al. reported a "three-layered" π -stacked ligand, namely 2,3-bis(6'-methyl-2'-pyridylmethylsulfanylmethyl) pyrazine, which was found to function, via intramolecular π stacking, as an exo-ditopic bridge upon binding to Ag(I) atoms [9]. This complex, together with our present work, suggests that the relatively weaker phenyl–phenyl, or more generally aromatic–aromatic interactions can be used to control the geometry of a ligand by delicate design.

N1a = 2.132(4); N1a-Ag-N1 = 173.3(3). Symmetry codes: (a) x, -y + 1/2, -z + 1/4. Except for the H atoms bound to N atoms, other H atoms are not shown for clarity. Key: N—dotted ball, C—empty ball, H—smaller empty ball, Ag—cross hatched ball

Conclusion

We have described in this paper the synthesis and crystal structures of two semi-rigid p-xylylene-bridged C^4 -linked bipyrazolyl ligands and their Ag(I) and Cu(II) complexes. Compared to our previously reported *m*-xylylene-bridged bipyrazoles, the *p*-xylylene-bridged analogs have different spatial arrangement for the two pyrazolyl rings and therefore different coordination chemistry. The 3,5-substituents of the pyrazole can be an important structural determinant in dictating the *cis*- or *trans*-conformations of the bipyrazoles. From the present structural study, we can see phenyl-phenyl interactions lead to the preference for trans-conformation of 3,5-diphenyl substituted bipyrazole (H_2L'), as observed in the structures of the Ag(I) complex and the free ligand. On the other hand, 3,5-dimethyl substituted bipyrazole (H₂L) exhibits greater flexibility in switching between two possible conformations, due to lack of such phenyl-phenyl interactions.

Experimental

The CHN microanalyses were obtained with a Flash EA 1112 elemental analyzer. IR spectra (KBr pellets) were recorded on a Niclolet Impact 420 FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Mass spectra were obtained with an Agilent 1100 series LC/MSD Trap XCT ion trap mass spectrometer. 2,3,5,6-tetramethyl-1,4-bis(bromomethyl)benzene was prepared by a literature method [10]. All other reagents were obtained commercially and used as received.

Preparation of 2,3,5,6-tetramethyl-1,4-bis[(3',5'dimethyl-1*H*-pyrazol-4'-yl)methylene] benzene (H₂L)

Potassium (0.59 g, 15 mmol) was dissolved in tert-butyl alcohol (60 mL). To the solution, pentane-2,4-dione (1.80 g, 18 mmol), 2,3,5,6-tetramethyl-1,4-bis(bromomethyl)benzene



(2.40 g, 7.5 mmol), and KI (0.34 g) were added successively. The mixture was stirred under nitrogen for 3 days, and then tert-butyl alcohol was distilled off. The residue was dissolved in CH₂Cl₂, and the solution was washed with water, dried over MgSO₄, and evaporated to dryness to obtain the bis-diketone—3,3'-(2,3,5,6-tetramethyl-1,4-phe-nylene)bis(methylene)dipentane-2,4-dione as a white solid. This bis-diketone was dissolved in chloroform (50 mL), and a solution of N₂H₄·H₂O (0.75 g, 15 mmol) in methanol (5 mL) was added slowly. The mixture was stirred at 50 °C for 12 h, then the solvent was distilled off, and the residue was washed with water. The crude product was recrystallized from ethanol to afford colorless needles of H₂L. Yield: 2.4 g, 90%.

C₂₂H₃₀N₄ (350.50) Found C 74.5, H 8.7, N 16.0; Calcd. C 75.4, H 8.6, N 16.0. ¹HNMR (400 MHz, DMSO-d₆): δ = 1.78 (s, 12H, CH₃−Ph), 2.09 (s, 12H, CH₃−pz), 3.70 (s, 4H, −CH₂−) ppm. **IR** (KBr): ν = 3,170s, 3,117s, 3,066m, 3,006w, 2,915s, 2,917s, 2,865s, 1,637w, 1,579 m, 1,515w, 1,464s, 1,411m, 1,379w, 1,298s, 1,199m, 1,157s, 1,053s, 1,009s, 829m, 794w, 744 m cm⁻¹. **MS**: m/z = 351.1 [M + H]⁺, 701.5 [M₂ + H]⁺.

Preparation of 2,3,5,6-tetramethyl-1,4-bis[(3',5'-diphenyl-1H-pyrazol-4'-yl)methylene] benzene (H₂L')

Potassium (0.59 g, 15 mmol) was dissolved in tert-butyl alcohol (60 mL). To the solution, dibenzoylmethane (4.10 g, 18 mmol), 2, 3, 5, 6-tetramethyl-1,4-bis(bromomethyl)benzene (2.40 g, 7.5 mmol), and KI (0.34 g) were added successively. The mixture was stirred under nitrogen for 3 days and then sucked under vacuum. The filter residue was washed successively with water and methanol and dried overnight in the air. The obtained bis-diketone was dissolved in chloroform (50 mL), and a solution of N_2H_4 · H_2O (0.75 g, 15 mmol) in methanol (5 mL) was added slowly. The mixture was stirred at 50 °C for 12 h, then the solvent was distilled off, and the residue was washed with aqueous methanol to afford the crude product, which was recrystallized from THF to yield colorless blocks of H_2L . Yield: 3.8 g, 85%.

 $\begin{array}{l} C_{42}H_{38}N_4\ (598.78)\ Found\ C\ 84.3,\ H\ 6.4,\ N\ 9.3;\ Calcd.\ C\\ 84.3,\ H\ 6.4,\ N\ 9.4.\ ^1\text{HNMR}\ (400\ MHz,\ CDCl_3):\ \delta\ =\ 1.60\\ (s,\ 12H,\ CH_{3}-),\ 3.88\ (s,\ 4H,\ -CH_{2}-),\ 7.13-7.26\ (m,\ 20H,\ Ph-H)\ ppm.\ IR\ (KBr):\ v\ =\ 3,228s,\ 3,056w,\ 3,021w,\ 2,947w,\ 1,605w,\ 1,561s,\ 1,491m,\ 1,434m,\ 1,253m,\ 1,221m,\ 1,134w,\ 970w,\ 768\ m,\ 700\ s\ cm^{-1}. \end{array}$

Preparation of $[Ag_2(H_2L)_2](BF_4)_2 \cdot 2H_2O(1)$

A solution of $AgBF_4$ (1.9 mg, 0.01 mmol) in acetonitrile (2 mL) was added to a solution of H_2L (3.5 mg, 0.01 mmol) in ethanol (2 mL). The resulting solution was allowed to evaporate for several days to afford colorless crystals in 15% (0.8 mg) yield.

 $C_{44}H_{60}N_8Ag_2B_2F_8$ ·2H₂O (1,124.33) Found C 47.0, H 5.6, N 10.3; Calcd. C 47.0, H 5.7, N 10.0. **IR** (KBr): v = 3,321 s, 2,919 s, 1,573 m, 1,522w, 1,438 m, 1,417 m, 1,383 m, 1,290 m, 1,184 s, 1,083 s (BF₄⁻), 1,040 s (BF₄⁻), 918 m, 694 m cm⁻¹.

Preparation of $[Ag(H_2L)(NO_3)]_n$ (2)

A solution of AgNO₃ (1.7 mg, 0.01 mmol) in methanol (2 mL) was added to a solution of H_2L (3.5 mg, 0.01 mmol) in ethanol (2 mL). The resulting solution was allowed to evaporate for 1 week to afford colorless crystals in 20% (1.1 mg) yield.

Table 1 Crystallographic data

	H_2L^\prime	1	2	4
Formula	$C_{42}H_{38}N_4$	C ₂₂ H ₃₂ AgBF ₄ N ₄ O	C22H30AgN5O3	C46H46AgBF4N4O
Mr	598.78	563.20	520.38	865.55
Crystal size (mm ³)	$0.42 \times 0.36 \times 0.13$	$0.30\times0.25\times0.20$	$0.30 \times 0.26 \times 0.24$	$0.32 \times 0.23 \times 0.19$
Crystal system	Monoclinic	Triclinic	Tetragonal	Triclinic
Space group	$P2_{1}/c$	P-1	I-42d	P-1
a (Å)	13.643 (3)	9.070 (3)	17.523 (3)	9.9614 (8)
<i>b</i> (Å)	13.343 (3)	11.267 (4)	17.523 (3)	13.0003 (11)
<i>c</i> (Å)	9.3064 (19)	14.919 (5)	16.220 (5)	17.5849 (15)
α (°)	90	69.376 (3)	90	69.8620 (10)
β (°)	103.65 (3)	79.445 (3)	90	86.3710 (10)
γ (°)	90	67.815 (3)	90	73.5370 (10)
$V(\text{\AA}^3)$	1646.3 (6)	1319.0 (7)	4980.3 (18)	2048.9 (3)
Ζ	2	2	8	2
T (K)	298	298	298	298
$D_{\text{calcd}} (\text{Mg/m}^3)$	1.208	1.418	1.388	1.403
$\mu \ (\mathrm{mm}^{-1})$	0.071	0.812	0.840	0.551
<i>F</i> (000) (e)	636	576	2,144	892
hkl range	$-11 \leq h \leq 18$	$-10 \le h \le 10$	$-23 \le h \le 21$	$-13 \leq h \leq 13$
	$-16 \le k \le 17$	$-13 \le k \le 13$	$-23 \le k \le 23$	$-17 \leq k \leq 17$
	$-12 \le l \le 12$	$-17 \le l \le 18$	$-21 \le l \le 21$	$-23 \le 1 \le 23$
Refl. Collected	12,601	8,807	18,745	18,646
Refl. Unique	3,983	4,742	3,079	9,867
	$(R_{int} = 0.0336)$	$(R_{int} = 0.0305)$	$(R_{int} = 0.0690)$	$(R_{int} = 0.0252)$
Param. refined	210	306	146	518
Restraints	0	2	0	5
Final R indices	R1 = 0.0578	R1 = 0.0536	R1 = 0.0591	R1 = 0.0541
$[I > 2\sigma(I)]$	wR2 = 0.1554	wR2 = 0.1755	wR2 = 0.1627	wR2 = 0.1370
GoF (F^2)	1.046	1.065	1.102	1.031
$\Delta \rho_{\rm fin}$ (max, min) e Å ⁻³	0.517, -0.462	1.776, -0.849	1.362, -0.573	0.821, -0.615

 $C_{22}H_{30}N_5AgO_3 H_2O$ (537.15) Found C 49.4, H 6.0, N 12.8; Calcd. C 49.2, H 6.0, N 13.0. **IR** (KBr): v = 3,189s, 3,082m, 2,919s, 1,578m, 1,334s (NO₃⁻), 1,320s (NO₃⁻), 1,188m, 1,056m, 1,039w, 1,013m, 825w cm⁻¹.

Preparation of $[Cu_2(H_2L)_4(SO_4)_2] \cdot 11H_2O$ (3)

A solution of H_2L (3.5 mg, 0.01 mmol) in ethanol (2 mL) was layered on the surface of an aqueous solution of CuSO₄·5H₂O (5.0 mg, 0.02 mmol) in a test tube. Dark blue crystals were obtained in 70% (3.4 mg) yield within several days.

 $C_{88}H_{142}N_{16}Cu_2S_2O_{19}$ (1,919.39) Found C 54.6, H 7.0, N 11.6, S 3.3; Calcd. C 55.1, H 7.5, N 11.7, S 3.3. **IR** (KBr): v = 3,420m, 3,237s, 3,083w, 2,924s, 2,762w, 1,637m, 1,577m, 1,526w, 1,440s, 1,383m, 1,315m, 1,291w, 1,184s (SO₄²⁻), 1,142s (SO₄²⁻), 1,109s (SO₄²⁻), 1,054s (SO₄²⁻), 974w, 803w, 615 m cm⁻¹.

Preparation of $\{[Ag(H_2L')]BF_4\}_n$ (4)

A solution of $AgBF_4$ (1.9 mg, 0.01 mmol) in acetonitrile (1 mL) was layered on the surface of a solution of H_2L' (6.0 mg, 0.01 mmol) in THF (3 mL) in a test tube. Colorless crystals were obtained in 15% (1.2 mg) yield within several days.

 $C_{42}H_{38}N_4AgBF_4$ (793.45) Found C 63.6, H 4.8, N 7.0; Calcd. C 63.6, H 4.8, N 7.1. **IR** (KBr): v = 3,290s, 3,058w,2,962w, 1,604w, 1,561m, 1,490s, 1,444s, 1,243m, 1,227m, 1,182s, 1,124s, 1,084s (BF₄⁻), 1,061s (BF₄⁻), 1,028s, 970s, 777m, 754m, 697 s cm⁻¹.

X-ray crystallography

Diffraction intensities were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo-K α radiation (0.71,073 Å). Absorption corrections were applied

using the multiscan program. The structures were solved by direct methods and refined by least squares techniques using the SHELXS-97 and SHELXL-97 programs [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically. In complex **3**, one S atom and two O atoms have been split into two parts with an occupancy factor of 0.5 due to the disorder of the sulfates.

Crystal data for H₂L', **1**, **2**, and **4** are summarized in Table 1. Because of the poor quality of crystal data of H₂L and **3**, only a preliminary structure analysis was carried out. However, the stoichiometry and heavy atom positions were unequivocally determined. For H₂L·2MeOH: C₂₂H₃₀N₄·2CH₃OH, monoclinic *P*2₁/*c*, *a* = 15.825(3), *b* = 5.2397(10), *c* = 15.519(3) Å, β = 108.97(3), *V* = 1,217.0(4) Å³, *S* = 1.363, *R*1 = 0.2781 for 2,389 reflections with *I* > 2 σ (*I*) and 143 parameters. For **3**: C₈₈H₁₄₀Cu₂N₁₆O₁₈S₂, monoclinic *C*2, *a* = 22.133(8), *b* = 19.368(4), *c* = 15.831(3) Å, β = 118.21(2)°, *V* = 5,980(3) Å³, *S* = 1.181, *R*1 = 0.1353 for 7,230 reflections with *I* > 2 σ (*I*) and 595 parameters.

CCDC 821902—821905 contain the supplementary crystallographic data for H_2L' , **1**, **2**, and **4**. 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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