Self-Assembly and Characterization of Grid-Type Copper(I), Silver(I), and Zinc(II) Complexes

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Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday

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The reactions of ligand **L**, which comprises two bidentate binding units, with copper(I), silver(I), and zinc(II) lead to the self-assembly of the expected supramolecular architectures **1**–**3**, respectively, of the [2×2] grid type, containing four ions in tetrahedral coordination sites. The grid-type structures are assigned on the basis of the spectroscopic data in solution, and confirmed in the solid state in the case of complex **2** by X-ray crystallography.

Introduction

Metal-directed self-assembly is a powerful synthetic methodology for supramolecular architectures that may exhibit novel physical and chemical properties with potential applications in supramolecular engineering, nanotechnology, biomedical inorganic chemistry, biological catalysis, and in the area of sensors. A variety of architectural types are known, such as, for example, inorganic double,[1–5] triple,[4,5] and quadruple[6] helicates, rotaxanes,[7–9] clusters,[10–12] racks,[13] cages,[14–16] grids[17–28] etc., based on ligand design and on the application of suitable coordination geometries for the assembly process. Among them, there is an increasing interest in grid-shaped complexes based on ligands containing oligopyridine-type groups and various transition metal ions. These grids are thermodynamically most stable when metal ions of tetrahedral coordination geometry are combined with a planar ligand containing bidentate binding subunits.[17,18,29–40] The first [2×2] grid type was obtained with copper(I) ions,[17] and copper(I) grid complexes have recently attracted much attention because of their well-defined supramolecular architectures and their interesting properties, such as special optical,[35] magnetic,[36] and electrochemical features or the atypical geometry of the grid structure.[37] Silver(I) has also been used as an assembling ion and, thanks to the flexibility of its coordination sphere, has yielded sophisticated coordination architectures such as [3×3][29] and $[(2\times5)_2]$[6] multinuclear grids. Such compounds form supramolecular systems that self-assemble into monolayer or bilayer crystalline films, which are of potential interest for microelectronics and nanotechnology.[38–41] Zinc is one of the most abundant metals in the human body, and fluorescent imaging has been proven to be the most suitable technique for its monitoring in vivo.[42,43]

One aim of our studies has been to explore further the possibilities of the self-assembly of supramolecular structures, in particular multinuclear grids from N-heterocyclic ligands. In this paper, we describe the synthesis and structural characterization of some polynuclear metal complexes prepared from the tetradentate ligand **L**, which contains pyridine and pyrimidine nitrogen donor atoms. The investigation of the complexation of ligand **L** with metal ions of preferred tetrahedral coordination geometry, such as Cu^{I}, Ag^{I}, and Zn^{II}, has revealed that the ligand is adequately preorganised for the assembly of tetranuclear [2×2] grid type complexes.

Results and Discussion

Synthesis of Ligand L

Ligand **L** possesses two N,N bidentate binding subunits for the complexation of ions with tetrahedral coordination geometry. It contains heterocyclic pyrimidine and pyridine units and was synthesised as outlined in Scheme 1.

2-Methyl-6-(trimethylstannyl)pyridine was obtained from 2-bromo-6-methylpyridine by a halogen/lithium exchange protocol at low temperature in THF with *n*-butyllithium, followed by quenching the pyridyllithium interme-

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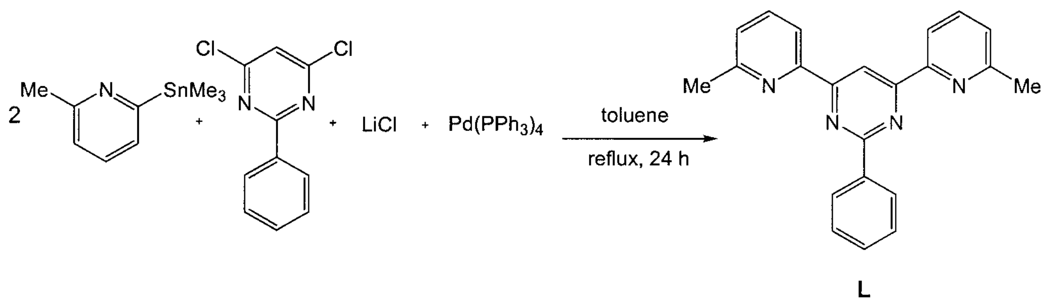


Scheme 1. Reaction scheme for the synthesis of ligand **L**.

diate with $ClSnMe_3$.[44,45] 4,6-Dichloro-2-phenylpyrimidine was prepared by treatment of $POCl_3$ with 2-phenylpyrimidine-4,6-diol.[46] The twofold Stille-type[47] coupling reaction of 2-methyl-6-(trimethylstannyl)pyridine with 4,6-dichloro-2-phenylpyrimidine in toluene using $[Pd(PPh_3)_4]$ as a catalyst furnished **L** in 54% yield after workup. The structure of ligand **L** was confirmed by NMR spectroscopy, FAB mass spectrometry, and elemental analysis. It was also structurally characterized by X-ray crystallography (Figure 1).

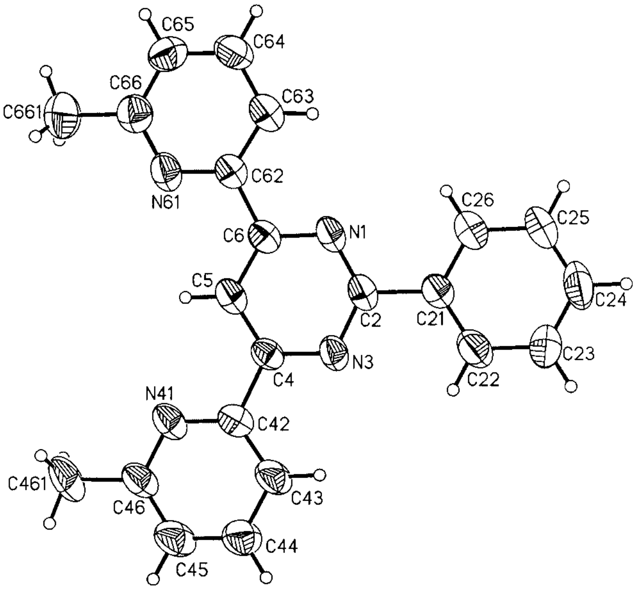


Figure 1. Anisotropic-ellipsoid representation of molecule **L** together with the numbering scheme. The ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheres of arbitrary radii.

Crystallographic Characterization of Ligand L

The crystal structure of the ligand molecule **L** shows that it is approximately planar (Figure 1). The four constituent rings are planar within the experimental error [maximum deviation from the least-squares plane is 0.012(3) Å], and the dihedral angles between their planes are small, up to 6.7(2)°. The mean values of aromatic C_{ar}–C_{ar} [1.373(9) Å], single C_{ar}–C_{ar} [1.489(6) Å], C_{ar}–C_{sp^3} [1.506(4) Å], and C_{ar}–N [1.340(4) Å] bond lengths are very close to typical values. The bond-angle pattern is also typical, with distortions from the ideal (120°) caused by the presence of heteroatoms and substituents. In the crystal structure, the principal intermolecular interaction is probably π-stacking between neighbouring molecules (approximately along the [610] direction); the mean distance between the π systems is 3.44 Å.

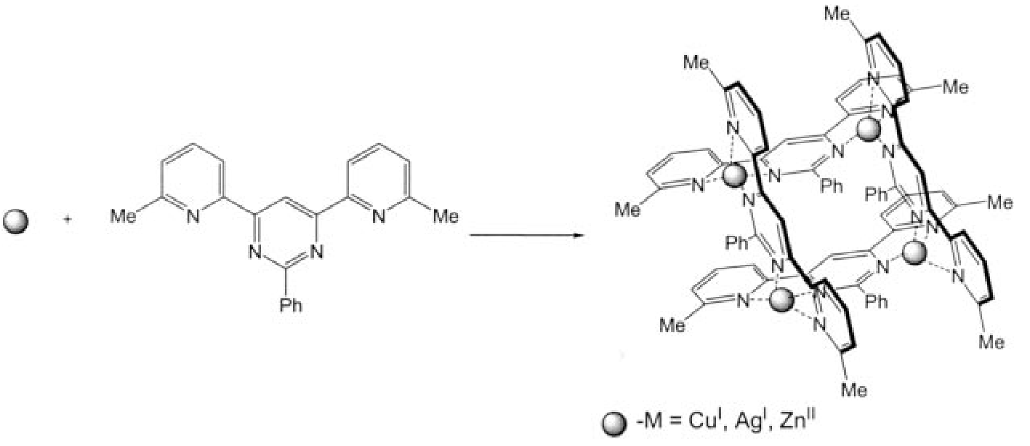
Synthesis and Characterization of the Complexes

Multitopic ligands with N,N-type donor sets allow the metal ion-directed assembly of coordination architectures. Thus, ligand **L** leads to the generation of the [2 × 2] grid architectures **1**–**3** with Cu^I, Ag^I, and Zn^{II}, respectively (Scheme 2).

The self-assembly of these complexes was achieved by reaction of **L** in acetonitrile, at room temperature, with tetrakis(acetonitrile)copper(I) hexafluorophosphate or the silver(I) and zinc(II) triflates. The complexation reactions were followed by ESI mass spectrometry and NMR spectroscopy.

The ^1H NMR spectra of the complexes show strongly shifted signals, as expected, and are strongly supportive of the grid-type structures. The signals of the symmetrically coordinated ligand in a single chemical and magnetic environment are in agreement with this type of structure. Interestingly, significant coordination-induced shifts of the signals are observed when the spectra of the complexes are compared to those of the uncomplexed ligand **L**.

ESI mass spectrometry is a highly sensitive and accurate analytical tool, which has been found to be particularly suitable for the identification of large metallosupramolecular architectures in solution, in which multiply charged ions are generated by sequential loss of counterions, resulting in characteristic isotopic patterns in the spectrum. The ESI-MS investigation of all complexes was performed with acetonitrile solutions at approximately 10^{-4} M. For example, the ESI mass spectrum of **2** shows peaks corresponding to multiply charged species at m/z = 785 (80%, $[AgL_2]^+$), 447 (100%, $[Ag_4L_4]^{4+}$), 339 (45%, $[L]^+$). These data confirm the presence of grid **2** in solution. The spectra of all the complexes include signals for $[ML_2]^{n+}$, $[M_4L_4]^{n+}$, and $[L]^+$, which means that significant dissociation of the grid complexes to mononuclear species and ligand molecules occurs in solution.



Scheme 2. Reaction scheme for the assembly of the [2×2] grid complexes **1**–**3**.

Solid-State Molecular Structure of Complex 2

Crystals of complex **2** were obtained by diffusion of diisopropyl ether into a solution of the complex in acetonitrile. The molecular structure of complex **2** was determined by X-ray crystallography at both 291 K and 100 K. It shows that it is of [2×2] grid-type (Figure 2), and is stable from 100 K to at least room temperature. We will discuss the low temperature structure here, but this discussion is equally valid for the structure determined at room temperature.

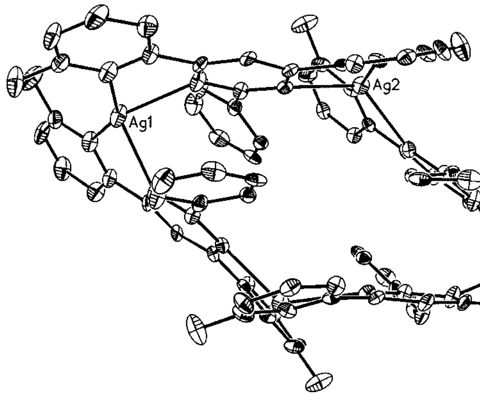


Figure 2. Anisotropic-ellipsoid representation of molecule **2** together with numbering scheme. The ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheres of arbitrary radii. The counterions, diisopropyl ether, and ligand molecules have been omitted for clarity.

The unit cell contains, besides the grid molecules, also the free ligand, counterion (triflate), and disordered solvent (diisopropyl ether) molecules. The grid is highly symmetrical: two independent silver ions, which lie on two different twofold axes, occupy the special positions of the space group *Ccca*. One of them occupies the Wyckoff position *e* (twofold axis along *x*), while the other occupies the Wyckoff position *f* (twofold axis along *y*). Thus, the symmetry-independent part of the grid contains two halves of silver ions and one ligand, and the rest is produced by symmetry operations. The free ligand molecule occupies yet another special position, that on the third twofold axis along the *z*-direction (atoms C2, C21, C24, and C5 lie at Wyckoff positions *g*).

Due to its symmetry, the grid is of rhombic shape and its size is within nanoscopic scale – the lengths of the diagonals are 1.18 and 1.92 nm. The formation of the grid causes significant changes in the shape of the ligand molecule. The free ligand molecule present in the crystal has a structure similar to that determined for **L**, with a maximum value of the dihedral angle between the least-squares of the aromatic planes of 9.9°. In contrast, the molecule in the complex is fairly folded. The dihedral angles between the planes of the central ring and terminal rings are 13.0°, 22.6°, and 40.0°, and the dihedral angles between the planes of the terminal rings are as large as 56.9°.

The Ag^{I} ions show distorted tetrahedral coordination, and the Ag···Ag distances are in the range 6.640–12.087 Å. The Ag–N distances can be divided into two classes: shorter [2.276(4) Å and 2.219(3) Å], to pyrimidine nitrogen atoms, and longer [2.449(5) Å and 2.471(5) Å], to pyridine nitrogen atoms. Selected bond lengths and angles are listed in Table 1.

Table 1. Selected geometrical parameters of the [2×2] grid-type complex **2**.[a]

Ag1–N1A	2.449(5)
Ag1–N61A	2.276(4)
Ag2–N41A	2.219(3)
Ag2–N3A	2.471(5)
$<(C–C)_{ar}>$	1.387(14)
$<(C–N)_{ar}>$	1.349(14)
N61A–Ag1–N61A^{i}	150.4(2)
N61A–Ag1–N1A^{i}	133.2(1)
N1A–Ag1–N61A	70.7(1)
N1A–Ag1–N1A^{i}	92.6(2)
N41A–Ag2–N41A^{ii}	164.3(2)
N3A–Ag2–N41A	72.2(2)
N41A–Ag2–N3A^{ii}	114.9(2)
N3A–Ag2–N3A^{ii}	130.1(2)

[a] Symmetry codes: ^{i} 1 – *x*, *y*, 1/2 – *z*; ^{ii} *x*, 1/2 – *y*, 1/2 – *z*.

The triflate anions are situated between the grid molecules and are held there by relatively strong and linear C–H···O hydrogen bonds (Table 2, Figure 3). Approximately planar, free ligand molecules lie between the grids, and interact with the aromatic rings by π-stacking interactions (the distance between the mean planes of the rings is about 3.4 Å). This intercalation occurs between two different grid fragments; an analogous intra-grid intercalation of the free ligand is observed, for example, in the copper(I) biphenanthroline grid structure.[33] There is additional free space in the crystal structure that is filled by disordered diisopropyl ether solvent molecules.

Table 2. Hydrogen bond data for **2** (low-temperature data).

D	H	A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
C461	H46C	$O3^{i}$	0.96	2.34	3.242(7)	157
C65A	H65A	$O2^{ii}$	0.93	2.34	3.275(7)	176
C661	H66B	$O3^{ii}$	0.96	2.48	3.429(7)	172
C5A	H5A	O1	0.92	2.48	3.380(6)	168
C43A	H43A	O1	0.92	2.46	3.303(7)	153

[a] Symmetry codes: ^{i} $1 - x$, y, $1/2 - z$; ^{ii} x, $1/2 - y$, $1/2 - z$.

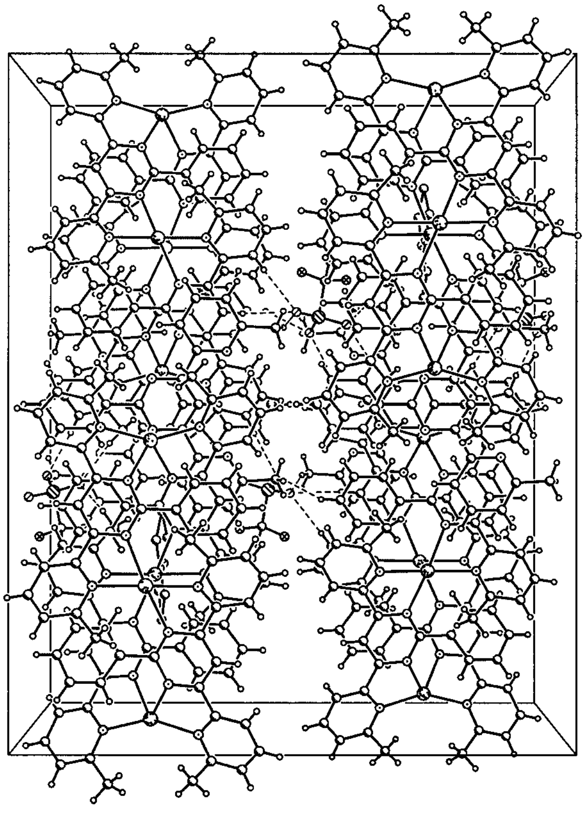


Figure 3. The content of the unit cell as seen approximately along the *a* direction (*z* across, *b* down). Weak hydrogen bonds are drawn as dashed lines.

Conclusions

The novel ligand **L** containing two bidentate N,N-binding subunits has been prepared and its solid state conformational properties characterized by X-ray crystallography. The reaction of **L** with Cu^{I}, Ag^{I}, and Zn^{II} results in the clean and quantitative formation of [2×2] grid-type complexes, which were characterized in solution on the basis of ESI mass spectrometry and ^{1}H NMR spectroscopy. The molecular structure of the Ag^{I} complex **2** was also investigated by X-ray crystallography, which confirmed that it indeed has a [2×2] grid-type architecture, with each metal ion tetrahedrally coordinated by two N,N donors.

The present results detail a particularly facile and rapid synthetic protocol for the preparation of [2×2] grid-type coordination scaffolds with Cu^{I}, Ag^{II}, and Zn^{II}. Related ligands and coordination arrays may be envisioned for the generation of various metallosupramolecular architectures.

Experimental Section

General: CH_3CN was freshly distilled under argon over CaH_2. 2-Methyl-6-(trimethylstannyl)pyridine[44,45] and 4,6-dichloro-2-phenylpyrimidine[46] were prepared according to the literature. The metal salts were used without further purification as supplied by Aldrich. NMR spectroscopic data were recorded on a Varian Gemini 300 MHz spectrometer, and were calibrated against the residual protonated solvent signal ($CDCl_3$: δ = 7.24 ppm; CD_3CN: δ = 1.94 ppm) and are given in ppm. Mass spectra were determined by FAB^+ using a ZAB-HF VG apparatus in a *m*-nitrobenzyl alcohol matrix and a Waters Micromass ZQ spectrometer in acetonitrile. The electronic absorption spectrum for ligand **L** in acetonitrile was measured on a Shimadzu UV 2401 PC spectrometer, with λ_{max} in nm and ε ($\times 10^4$) in $M^{-1}cm^{-1}$. The luminescence spectrum for ligand **L** in CH_3CN was recorded using a Perkin–Elmer MPF-3 spectrofluorimeter. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyzer. Melting points were recorded on an Electrothermal Digital melting point apparatus.

4,6-Bis(6-methylpyridin-2-yl)-2-phenylpyrimidine (L): 2-Methyl-6-(trimethylstannyl)pyridine (2.0 g, 8 mmol) and degassed toluene (25 mL) were added consecutively, by syringe, to a mixture of 4,6-dichloro-2-phenylpyrimidine (0.6258 g, 3 mmol), $[Pd(PPh_3)_4]$ (0.10 g, 0.9 mmol), and LiCl (0.68 g, 16 mmol) under argon. The reaction was refluxed and stirred at 120 °C for 24 h, and the toluene evaporated in a water bath under reduced pressure. The residue was then purified by column chromatography on alumina and eluted with dichloromethane/*n*-hexane (4:6); yield: 0.50 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.27 (s, 1 H, H-5), 8.72 (t, J = 7.9 Hz, 1 H, H-4′′′), 8.50 (d, J = 7.6 Hz, 2 H, H-2′′′,6′′′), 7.79 (t, J = 7.6 Hz, 2 H, H-4′,4′′), 7.54 (m, J = 5.2 Hz, 4 H, H-3′,3′′,5′,5′′), 7.20 (t, J = 7.9 Hz, 2 H, H-3′′′,5′′′), 2.66 (s, CH_3) ppm. ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 164.4, 163.9, 158.4, 154.1, 138.0 (CH), 137.2 (CH), 130.6, 128.5 (CH), 128.4 (CH), 124.9 (CH), 119.0 (CH), 111.6 (CH), 24.6 (CH_3). FAB-MS: *m*/*z* (%) = 339.2 (100) [L + H]. UV/Vis (CH_3CN): λ = 233, 272.5, 281.5, 318 nm. Luminescence: $\lambda_{ex.}$ = 298 nm, $\lambda_{em.}$ = 356 nm. $C_{22}H_{18}N_4$ (338.4): calcd. C 78.08, H 5.36, N 16.56; found C 77.99, H 5.33, N 16.42. M.p. 170 °C.

Cu Complex 1: An equimolar mixture of $[Cu(CH_3CN)_4]PF_6$ (11.0 mg, 30 µmol) and ligand **L** (10.0 mg, 30 µmol) in MeCN (5 mL) was stirred at room temperature for 24 h. The solvent was then evaporated under reduced pressure to give a quantitative yield of **1** as a purple-violet powder. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.16 (s, 1 H, H-5), 8.71 (t, 1 H, H-4′′′), 8.59 (d, 2 H, H-2′′′,6′′′), 8.01 (t, 2 H, H-4′,4′′), 7.55 (m, 4 H, H-3′,3′′,5′,5′′), 7.26 (t, 2 H, H-3′′′,5′′′), 2.68 (s, CH_3) ppm. ESI-MS: *m*/*z* = 739 $[CuL_2]^+$, 401 $[Cu_4L_4]^{4+}$, 339 $[L]^+$. $Cu_4(L)_4(PF_6)_4$ (2187.7): calcd. C 48.31, H 3.32, N 10.24; found C 49.01, H 3.33, N 9.98.

Ag Complex 2: A solution of ligand **L** (10.0 mg, 30 µmol) and Ag(CF_3SO_3) (7.6 mg, 30 µmol) in MeCN (5 mL) was stirred at room temperature for 24 h. The white complex **2** was isolated in quantitative yield by evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.21 (s, 1 H, H-5), 8.73 (t, 1 H, H-4′′′), 8.55 (d, 2 H, H-2′′′,6′′′), 7.91 (t, 2 H, H-4′,4′′), 7.58 (m, 4 H, H-3′,3′′,5′,5′′), 7.45 (t, 2 H, H-3′′′,5′′′), 2.69 (s, CH_3) ppm. ESI-MS: m/z = 785 [Ag$\mathbf{L}_2$]$^+$, 447 [$Ag_4\mathbf{L}_4$]$^{4+}$, 339 [**L**]$^+$. $Ag_4(\mathbf{L})_4(CF_3SO_3)_4\cdot 2\mathbf{L}\cdot C_6H_{14}O$ (3160.4): calcd. C 53.97, H 3.89, N 10.64, S 4.06; found C 54.39, H 3.83, N 10.65, S 4.10.

Zn Complex 3: An equimolar mixture of $Zn(CF_3SO_3)_2$ (13.3 mg, 39 µmol) and ligand **L** (14.2 mg, 39 µmol) in MeCN (5 mL) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to yield a pale-green complex **3** in quantitative yield. ESI-MS: m/z = 889 {[Zn(**L**)$_2$](CF_3SO_3)}$^+$, 553 {[Zn_4(**L**)$_4$](CF_3SO_3)$_4$}$^{4+}$, 371 [Zn(**L**)$_2$]$^{2+}$, 339 [**L**]$^+$, 254 {[Zn_4(**L**)$_4$](CF_3SO_3)}$^{7+}$. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.32 (s, 1 H, H-5), 8.64 (t, 1 H, H-4′′′), 8.52 (d, 2 H, H-2′′′,6′′′), 7.99 (t, 2 H, H-4′,4′′), 7.83 (m, 4 H, H-3′,3′′,5′,5′′), 7.60 (t, 2 H, H-3′′′,5′′′), 2.75 (s, CH_3) ppm. $Zn_4(\mathbf{L})_4(CF_3SO_3)_8$ (2807.7): calcd. C 41.07, H 2.58, N 7.98, S 9.14; found C 41.12, H 2.49, N 7.77, S 9.28.

Crystal Structure Determination of Ligand and Complex 2: Diffraction data for **L** were collected at 291(1) K and for **2** at both 291(1) and 100(1) K by the ω-scan technique up to $2\theta = 60°$, on a KUMA-KM4CCD diffractometer[48] with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz-polarization effects,[49] as well as for absorption, with SORTAV.[50] Unit-cell parameters were determined by the least-squares fit of 2258 (**L**), 4514 (**2**-RT), and 3783 (**2**-LT) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SHELXS97[51] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.[52] Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed geometrically in idealized positions and refined as rigid groups, with U_{iso} of the hydrogen atoms set as 1.2 (1.3 for CH_2 and CH_3 groups) times U_{eq} of the appropriate carrier atom. Relevant crystal data are listed in Table 3, together with refinement details.

Table 3. Crystal data, data collection, and structure refinement.

Compound	L	2
Formula	$C_{22}H_{18}N_4$	$C_{142}H_{122}Ag_4F_{12}N_{24}O_{13}S_4$
Formula mass	338.40	3160.35
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$Ccca$
a [Å]	4.2565(8)	17.4365(9)
b [Å]	16.8939(16)	30.4319(18)
c [Å]	24.1686(17)	24.5520(13)
V [Å^3]	1737.9(4)	13027.9(12)
Z	4	2
$D_{calcd.}$ [g cm^{-3}]	1.293	1.585
$F(000)$	712	6288
μ [mm^{-1}]	0.079	0.7471
Crystal size [mm]	0.5 × 0.08 × 0.07	0.15 × 0.08 × 0.08
Θ range [°]	2.94–29.44	2.82–29.57
hkl range	$-5 \le h \le 2$	$-23 \le h \le 21$
	$-23 \le k \le 23$	$-40 \le k \le 40$
	$-33 \le l \le 33$	$-33 \le l \le 20$
Reflections collected	11688	27152
Reflections unique (R_{int})	2576 (0.074)	8263 (0.094)
Final $R(F)$ [$I > 2\sigma(I)$]	0.058	0.065
Final $wR(F^2)$ [all data]	0.096	0.095
Goodness of fit	1.060	0.967
Max/min $\Delta\rho$ [eÅ^{-3}]	0.14/–0.14	0.87/–0.51

CCDC-264396 (for **1**), -264397 (for **2**-RT), and -264398 (for **2**-LT) 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.

Acknowledgments

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[1] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569.
[2] M. Barboiu, G. Vaughan, N. Kyritsakas, J.-M. Lehn, *Chem. Eur. J.* **2003**, *9*, 763–769.
[3] J. E. Aguado, M. J. Calhorda, P. J. Costa, O. Crespo, V. Félix, M. C. Gimeno, P. G. Jones, A. Laguna, *Eur. J. Inorg. Chem.* **2004**, 3038–3047.
[4] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497.
[5] R. Krämer, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703–706.
[6] P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510–4517.
[7] P. N. W. Baxter, H. Sleiman, J.-M. Lehn, K. Rissanen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1294–1296.
[8] H. Sleiman, P. N. W. Baxter, J.-M. Lehn, K. Airola, K. Rissanen, *Inorg. Chem.* **1997**, *36*, 4734–4742.
[9] M. C. Jimenez-Molero, Ch. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Eur. J.* **2002**, *8*, 1455–1466.
[10] L. J. Ashfield, A. R. Cowley, J. R. Dilworth, P. S. Donelly, *Inorg. Chem.* **2004**, *43*, 4121–4123.
[11] A. L. Pickering, D.-L. Long, L. Cronin, *Inorg. Chem.* **2004**, *43*, 4953–4961.
[12] F. Bramsen, A. D. Bond, C. J. McKenzie, R. G. Hazell, B. Moubaraki, K. S. Murray, *Chem. Eur. J.* **2005**, *11*, 825–831.
[13] R. L. Paul, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, Z. R. Reeves, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2000**, 845–851.
[14] A. M. Garcia, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1234–1238.
[15] M. Yoshizawa, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 10454–10459.
[16] M. Yoshizawa, Y. Takeyama, T. Kusukawa, M. Fujita, *Angew. Chem. Int. Ed.* **2002**, *41*, 1347–1349.
[17] M.-T. Youinou, N. Rahmouni, J. Fischer, J. A. Osborn, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 733–735.
[18] P. N. W. Baxter, J.-M. Lehn, K. Rissanen, *Chem. Commun.* **1997**, 1323–1324.
[19] J. Rojo, M. Ruben, E. Breuning, J.-P. Giesselbrecht, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2000**, *39*, 4139–4142.
[20] E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegelius, K. Rissanen, *Angew. Chem. Int. Ed.* **2000**, *39*, 2504–2505.
[21] H. Oshio, H. Onodera, O. Tamada, H. Mizutani, T. Hikichi, T. Ito, *Chem. Eur. J.* **2000**, *6*, 2523–2530.
[22] P. N. W. Baxter, R. G. Khoury, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4140–4148.
[23] A. Marquis, J.-P. Kintzinger, R. Graff, P. N. W. Baxter, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2002**, *41*, 2760–2764.
[24] J. P. Plante, P. D. Jones, D. R. Powell, T. E. Glass, *Chem. Commun.* **2003**, 336–337.
[25] M. Ruben, E. Breuning, M. Barboiu, J.-P. Gisselbrecht, J.-M. Lehn, *Chem. Eur. J.* **2003**, *9*, 291–299.
[26] J. Hausmann, G. B. Jameson, S. Brooker, *Chem. Commun.* **2003**, 2992–2993.

[27] V. Patroniak, P. N. W. Baxter, J.-M. Lehn, M. Kubicki, M. Nissinen, K. Rissanen, *Eur. J. Inorg. Chem.* **2003**, 4001–4009.
[28] L. H. Uppadine, J.-P. Gisselbrecht, J.-M. Lehn, *Chem. Commun.* **2004**, 718–719.
[29] P. N. W. Baxter, J.-M. Lehn, J. Fisher, M.-T. Youinou, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2284–2287.
[30] P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, D. Fenske, *Chem. Commun.* **1997**, 2231–2232.
[31] P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1978–1981.
[32] S. Toyota, C. R. Woods, M. Benaglia, R. Haldimann, K. Wärnmark, K. Hardcastle, J. S. Siegel, *Angew. Chem. Int. Ed.* **2001**, *40*, 751–754.
[33] A. Marquis, J.-P. Kintzinger, R. Graff, P. N. W. Baxter, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2002**, *41*, 2760–2764.
[34] R. Ziessel, L. Charbonnière, M. Cesario, T. Prangé, H. Nierengarten, *Angew. Chem. Int. Ed.* **2002**, *41*, 975–979.
[35] R. Hoogenboom, G. Kickelbick, U. S. Schubert, *Eur. J. Org. Chem.* **2003**, 4887–4896.
[36] Y. Lan, D. K. Kennepohl, B. Moubaraki, K. S. Murray, J. D. Cashion, G. B. Jameson, S. Brooker, *Chem. Eur. J.* **2003**, *9*, 3772–3784.
[37] J. R. Nitschke, M. Hutin, G. Bernardinelli, *Angew. Chem. Int. Ed.* **2004**, *43*, 6724–6727.
[38] I. Weissbuch, P. N. W. Baxter, S. Cohen, H. Cohen, K. Kjaer, P. B. Howes, J. Als-Nielsen, G. S. Hanan, U. S. Schubert, J.-M. Lehn, L. Leiserowitz, M. Lahav, *J. Am. Chem. Soc.* **1998**, *120*, 4850–4860.
[39] I. Weissbuch, P. N. W. Baxter, I. Kuzmenko, H. Cohen, S. Cohen, K. Kjaer, P. B. Howes, J. Als-Nielsen, J.-M. Lehn, L. Leiserowitz, M. Lahav, *Chem. Eur. J.* **2000**, *6*, 725–734.
[40] M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662.
[41] B. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem. Eur. J.* **2005**, *11*, 454–463.
[42] P. Jiang, Z. Guo, *Coord. Chem. Rev.* **2004**, *248*, 205–229.
[43] N. C. Lim, H. C. Freake, C. Brückner, *Chem. Eur. J.* **2005**, *11*, 38–49.
[44] P. Jutzi, U. J. Gilge, *J. Organomet. Chem.* **1983**, *246*, 163–168.
[45] G. V. Long, S. E. Boyd, M. M. Harding, I. E. Buys, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **1993**, 3175–3180.
[46] K. Burdeska, H. Fuhrer, G. Kabas, A. E. Siegriest, *Helv. Chim. Acta* **1981**, *64*, 113–152.
[47] J. K. Stille, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524.
[48] Oxford Diffraction (**2003**). *CrysAlisCCD*, User Guide v.171. Oxford Diffraction Poland Sp., Wrocław, Poland.
[49] Oxford Diffraction (**2003**). *CrysAlisRed*, CCD data reduction GUI v.171. Oxford Diffraction Poland Sp., Wrocław, Poland.
[50] R. H. Blessing, *J. Appl. Crystallogr.* **1989**, *22*, 396.
[51] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–476.
[52] G. M. Sheldrick, *SHELX97 – Programs for Crystal Structure Analysis* (Release 97-2). Institut für Anorganische Chemie der Universität, Tammanstrasse 4, 3400 Göttingen, Germany, **1998**.

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