Self-Assembly and Characterization of Multimetallic Grid-Type Lead(II) Complexes

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Abstract: The self-assembly of the ligands **1a–d**, containing tridentate binding subunits, with lead(II) ions lead to the formation of the supramolecular inorganic architectures **2–4** of [2 × 2], [3 × 3], and [4 × 4] grid-type containing four, nine, and sixteen lead(II) ions, respectively, in octahedral coordination sites. The structures have been assigned on the basis of the spectroscopic data in solution, and confirmed in the case of **2a** in the solid state by X-ray radiocrystallography. The entities **2–4** display specific arrays of metal ions and are of potential interest for the development of devices for molecular electronics. Their formation, in particular that of **4**, stresses the power of correctly designed self-assembly processes to generate highly complex architectures of well-defined geometry and nanometric size in a spontaneous but controlled fashion, without having to resort to nanofabrication procedures.

Keywords: grid-type structures · lead · N ligands · self-assembly · terpyridines

Introduction

The generation of complex supramolecular architectures may be achieved through self-assembly and self-organization processes based on suitably instructed components subject to specific interaction schemes.[1] Such is the case for the precise formation of biological superstructures from molecular components displaying highly directed mutual recognition. Various types of artificial organic and inorganic systems undergoing self-assembly have been devised in recent years.[1–3] In particular, the generation of inorganic supramolecular architectures is based on ligands that contain suitable binding sites in a correct arrangement; these may be read by metal ions following the algorithm defined by their coordination geometry.[1] The resulting entities may present a variety of new chemical and physical properties, different from those shown by the ligands and metal ions themselves, and they are potential candidates as components of functional nanostructures. Among the different types of superstructures that may be imagined, entities in which metal ions are arranged in a grid-type fashion are of special interest, in particular in view of an eventual incorporation into information storage devices that such arrays suggest.

Square $[n \times n]$[4a] and rectangular $[n \times m]$[4b] grids based on metal ions of tetrahedral coordination geometry have been obtained, as well as [2 × 2] grids containing ions of octahedral coordination.[5] In view of both their basic interest and the potential applications that such entities may present, further exploration of the self-assembly of grids of various sizes, which incorporate different numbers and types of metal ions, is warranted.

Herein we describe the synthesis and characterization of the extended inorganic grid-type structures **2**, **3**, and **4** formed by self-assembly from ligands **1a–1d**, containing terpyridine type subunits, and Pb^{II} ions as metal centers (Scheme 1). The synthesis of the ligands **1a–1d** has been reported previously by our laboratory.[6, 7] Pb^{II} ions were selected as assembly sites because these large ions were expected to distort the ligands less than the coordination of the comparatively small transition metal ions[8] and to give, therefore, access to novel grid structures.

Results and Discussion

Self-assembly and characterization of the [2 × 2]–Pb^{II}_4 grid-type complexes 2: The self-assembly reaction to obtain complex **2b** was carried out as follows: ligand **1b** was mixed with a stoichiometric amount of $Pb(OTf)_2$ in acetonitrile and the mixture was stirred overnight at room temperature.

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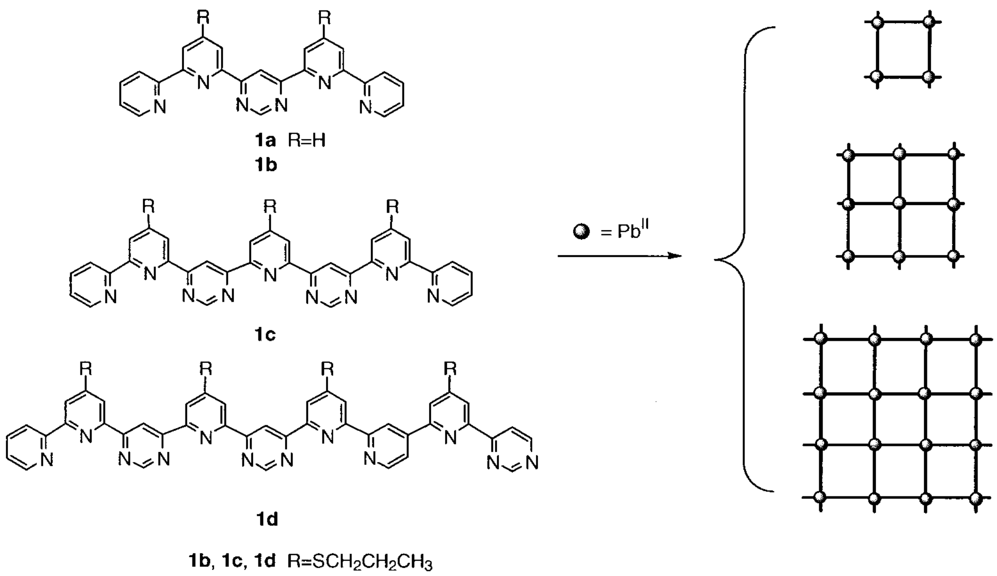
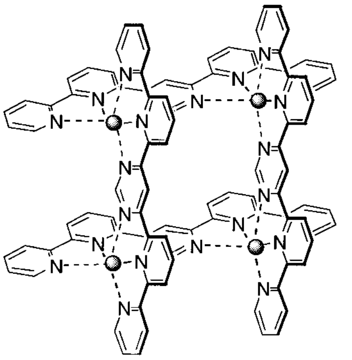
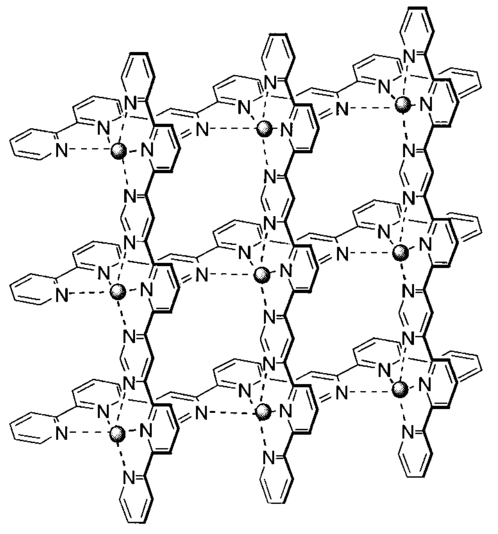


Scheme 1. Structure of ligands **1a**–**1d** and schematic representation of their self-assembly into inorganic [*n* × *n*] grid-type structures with lead(II) ions.



2a
2b (ligand **1b**, R omitted)



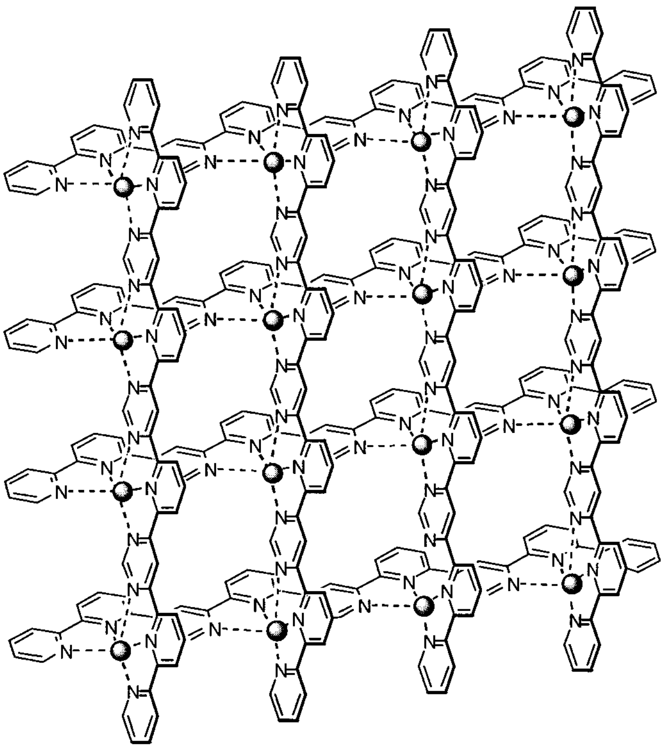
3 (ligand **1c**, R omitted)

Removal of the solvent under reduced pressure yielded a yellow powder. The ^{1}H NMR spectrum of the crude mixture confirmed the presence of only one compound, and it was concluded that the formation of the complex was quantitative. The complex was further purified by diethyl ether precipitation from a solution in acetonitrile.

Complex **2b** was characterized by ^{1}H, ^{13}C, and ROESY NMR spectroscopy, and FAB mass spectrometry. The FAB mass spectrum of **2b** displayed only two main peaks at *m/z* (%) = 4019.3 (20) and 3870.1 (10), which correspond to the species $\{[Pb_4\mathbf{1b}_4](OTf)_7\}^{1+}$ and $\{[Pb_4\mathbf{1b}_4](OTf)_6\}^{2+}$, respectively, indicating the formation of a tetrameric complex. The ^{1}H NMR spectrum of **2b** showed only one set of signals corresponding to the four ligands; these were assigned from the two-dimensional ROESY. The simple pattern indicated a highly symmetric structure, with ligand **1b** situated in a single chemical and magnetic environment.

Complex **2a**, based on the ligand **1a**,[7] was also prepared following the procedure described above. The complex obtained was identified by ^{1}H NMR and FAB mass spectrometry. Single crystals of this complex of sufficient quality were obtained by slow diffusion of diethylether into saturated acetonitrile solutions, and its structure was determined by X-ray crystallography. The crystal structure showed the complex to have a [2 × 2] grid-type structure and to be composed of four ligands **1b**, four lead cations, and four

Abstract in French: *L'autoassemblage des ligands **1a**–**d**, contenant des centres de coordination tridentates, avec des ions plomb(II) conduit à la formation des architectures inorganiques **2**–**4** de type grille d'ordre [2 × 2], [3 × 3] et [4 × 4] contenant quatre, neuf et seize ions Pb^{II} respectivement, dans des sites de coordination octaédriques. La structure de ces espèces a été attribuée sur la base de données spectroscopiques et confirmée dans le cas de **2a** en phase cristalline par radiocristallographie. Les complexes **2**–**4** présentent des arrangements spécifiques d'ions métalliques d'intérêt potentiel en électronique moléculaire. Leur formation, en particulier celle de la grille [4 × 4] **4**, démontre la puissance des processus d'autoassociation programmée pour la génération d'architectures de géométrie définie de taille nanométrique de façon spontanée mais controlée, sans devoir recourir à des procédés de nanofabrication.*



4 (ligand **1d**, R omitted)

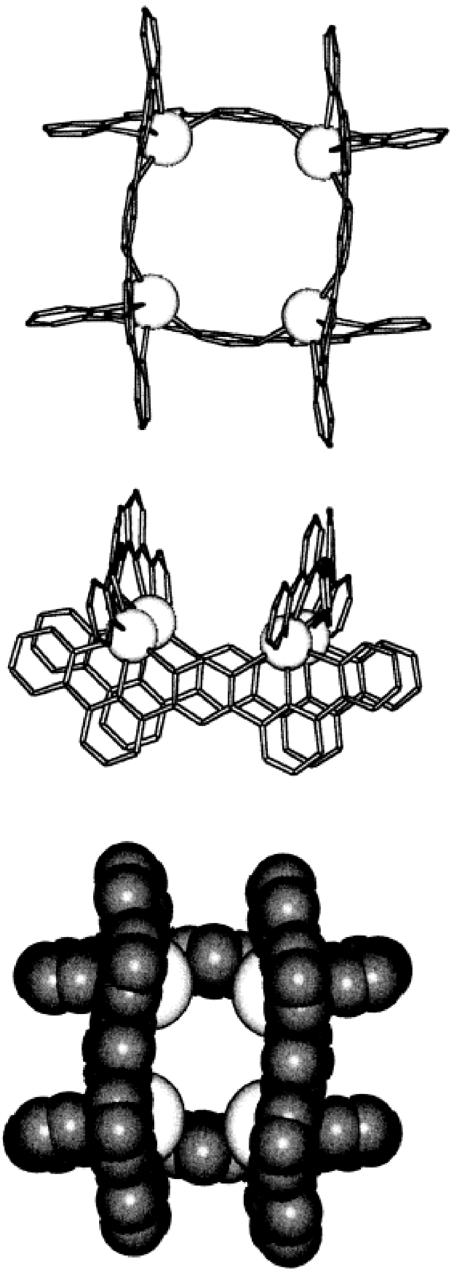


Figure 1. Crystal structure of the $[2\times2]{-}Pb^{II}_4$ grid-type complex **2a**: top view (top); side view (center); top-view, space-filling representation (bottom); triflate anions omitted for clarity.

triflate counteranions located in two positions (Figures 1 and 2). The ligands are somewhat warped and the metal ions lie almost in a plane and form a square. The average Pb–N distances are 2.58 Å (pyridine N) and 2.77 Å (pyrimidine N); they are similar to the lead–nitrogen distances already reported in literature.[9] The average Pb–Pb distance is 6.51 Å.

The coordination geometry around lead reveals a hemi-directed structure, in which the bonds to the ligands are directed towards only one part of the coordination sphere. The presence of a gap in the angular distribution of ligands can indicate the existence of a stereochemically active electronic lone pair in the lead ions.[10] In the structure of **2b**, the open faces of the metal ions are oriented towards the interior of the complex and occupied by the coordinated triflate counter anions (Figure 2).

The structure of **2a** differs significantly from that of $[2\times2]$ grids of transition metal ions, which display a distorted octahedral coordination to the perpendicularly oriented ligands.[5, 11] Although the average M–M distance is rather similar in these complexes (imposed by the distances between the coordination sites), the M–N distances are, as expected, much longer for the large $M = Pb^{II}$ ions. For example, for Co^{II} grid-type complexes, the average Co–N distances are 2.10 Å (pyridine N) and 2.23 Å (pyrimidine N).[5a]

Formation and detection of the $[3\times3]{-}Pb^{II}_9$ grid-type complex 3: The successful formation of complex **2** suggested that it might be possible to achieve the self-assembly of a larger grid-type structure **3**. Mixing equimolecular amounts of $Pb(OTf)_2$ and ligand **1c** in acetonitrile, and stirring overnight, led to a mixture that was analyzed by ^1H NMR and ES mass spectrometry. The ^1H NMR spectrum observed in deuterated acetonitrile agrees with the formation mainly of the desired complex **3** (Figure 3). Ligand **1c** appears in two different chemical environments as indicated by the presence of two sets of signals in a ratio of 1:2. This corresponds to four outer ligands and two inner ligands as expected for a $[3\times3]{-}Pb^{II}_9$ grid-type structure. However, when the spectrum was run in deuterated nitromethane, a mixture of species was detected. These observations could be due to the difference in coordinating character of the two solvents, the exchange processes between the different species being slower in the less-coordinating CD_3NO_2 solvent. Attempts to determine the ^{207}Pb NMR spectrum of **3** were unsuccessful; no signal was observed, probably owing to Pb^{II} exchange processes in solution.

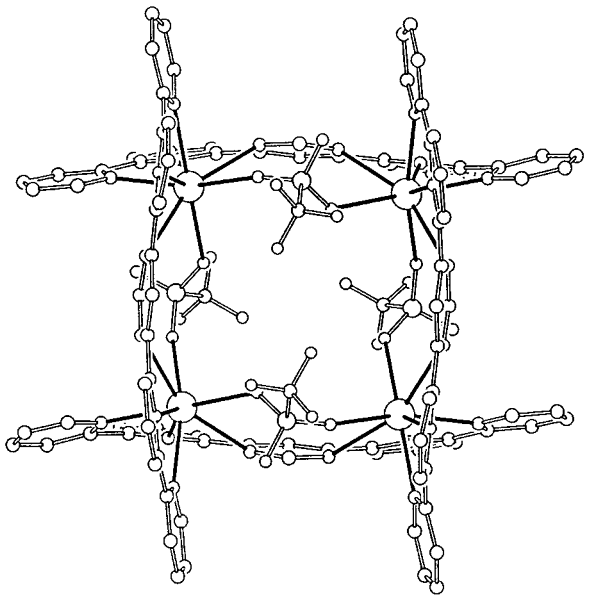


Figure 2. Crystal sructure of complex **2a**, ball-and-stick representation (top view), showing one set of the four triflate anions coordinated to the Pb^{II} centers.

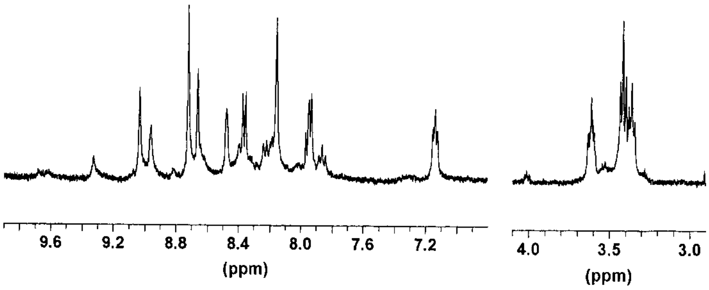


Figure 3. 400 MHz ^{1}H NMR spectrum of a CD$_3$CN solution of the grid complex **3** as formed by self-assembly from ligand **1c** and lead(II) triflate; for signal assignment, see Experimental Section.

ES mass spectrometry measurements provided evidence for the presence of complex **3** as the major product in the reaction mixture, accompanied by the $[3\times 2]$–Pb$^{II}_6$ grid-type complex as minor species. These spectrometric data indicate that the grid complex **3** does indeed form preferentially, but in equilibirum with other, minor complexes. Unfortunately, crystals suitable for X-ray crystallographic analysis could not be obtained.

Formation and characterization of the $[4\times 4]$–Pb$^{II}_{16}$ grid-type complex 4: The formation of the hexadecanuclear $[4\times 4]$–Pb$^{II}_{16}$ grid complex **4** was carried out following the same protocol as described for the $[2\times 2]$ and $[3\times 3]$ grids **2** and **3**. A mixture of stoichiometric amounts of ligand **1d** and Pb(OTf)$_2$ in acetonitrile was stirred overnight at room temperature. Evaporation of the solvent under reduced pressure yielded a yellowish solid. The ^{1}H NMR spectrum of this material, without further purification, showed that it consisted of *only one compound*, indicating that the reaction was quantitative.

The grid-type complex **4** was characterized by ^{1}H and ^{207}Pb NMR spectroscopy, and ES mass spectrometry. The ES mass spectrum of compound **4** showed peaks that correspond to multiply charged species possessing the correct composition: $\{[\mathrm{Pb}_{16}\mathbf{1d}_8](\mathrm{OTf})_n\}^{(32-n)+}$, with $n = 23-27$ (see Experimental Section).

The ^{1}H NMR spectrum indicated a high symmetry; it displayed only two different sets of signals for ligands **1d** in a ratio of 1:1. This pattern is consistent with the existence in complex **4** of four outer and four inner ligands **1d**, which are located in two different environments (Figure 4; for signal assignment see Experimental Section).

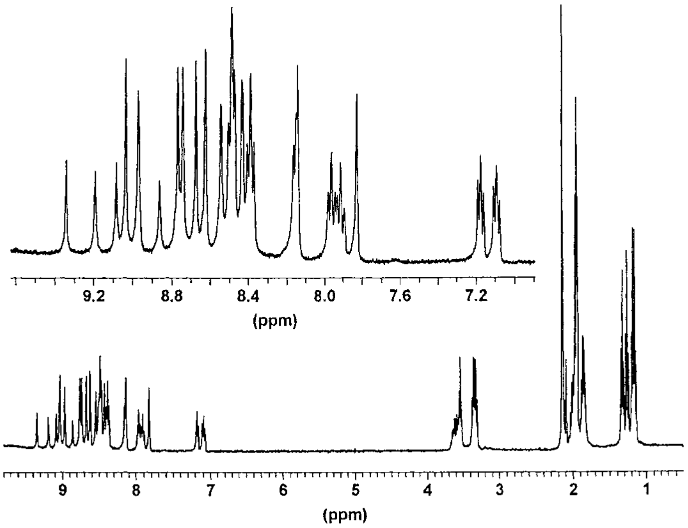


Figure 4. 400 MHz ^{1}H NMR spectrum of a CD$_3$CN solution of the hexadecanuclear grid-type complex **4** as obtained by self-assembly from ligand **1d** and lead(II) triflate; for signal assignment, see Experimental Section.

The ^{207}Pb NMR provided decisive information. It showed three signals in a 1:2:1 ratio, corresponding to lead cations in three different chemical environments: four at the corners, four in the interior and eight at positions 2 and 3 on the edges. The nature of the nitrogens in the binding sites and the number of neighboring Pb^{207} ions determines the sequence of chemical shifts in the ^{207}Pb NMR spectrum. The ^{109}Ag NMR signals of a $[3\times 3]$–Ag$_9^+$ complex of grid-type architecture indicated a decreasing shift (lower ppm values) with increasing number of less basic nitrogen sites and neighboring ions.[4a] On this basis, in the spectrum represented in Figure 5 the signals from left to right may be assigned as follows [Pb$_{\mathrm{position}}$ (number of vicinal Pb ions, type and number of nitrogen sites)]: Pb$_{\mathrm{vertex}}$ (2, py$_4$, pym$_2$), Pb$_{\mathrm{edge}}$ (3, py$_3$, pym$_3$), and Pb$_{\mathrm{interior}}$ (4, py$_2$, pym$_4$). Thus, both the relative intensity and the chemical shift sequence of the signals agree with the $[4\times 4]$ grid structure **4**.

All the spectrometric data indicate that the self-assembly of ligand **1d** with lead(II) ions leads to the exclusive formation of the hexadecanuclear $[4\times 4]$–Pb$^{II}_{16}$ grid-type complex **4** in solution. It amounts to the correct assembly of 24 components through the formation of 96(!) coordination bonds in a single operation. Unfortunately, it has not yet been possible to obtain crystals suitable for the determination of the solid-state structure of complex **4** by X-ray crystallography.

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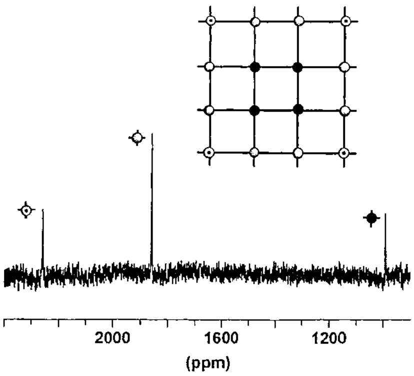


Figure 5. 41.813 MHz ^{207}Pb NMR spectrum of a solution (approximately 1 mM) of the [4 × 4]–Pb$^{II}_{16}$ grid complex **4** in CD$_3$CN. The chemical shifts are given with respect to a saturated solution of lead triflate in CD$_3$CN; for signal assignment, see text.

Conclusion

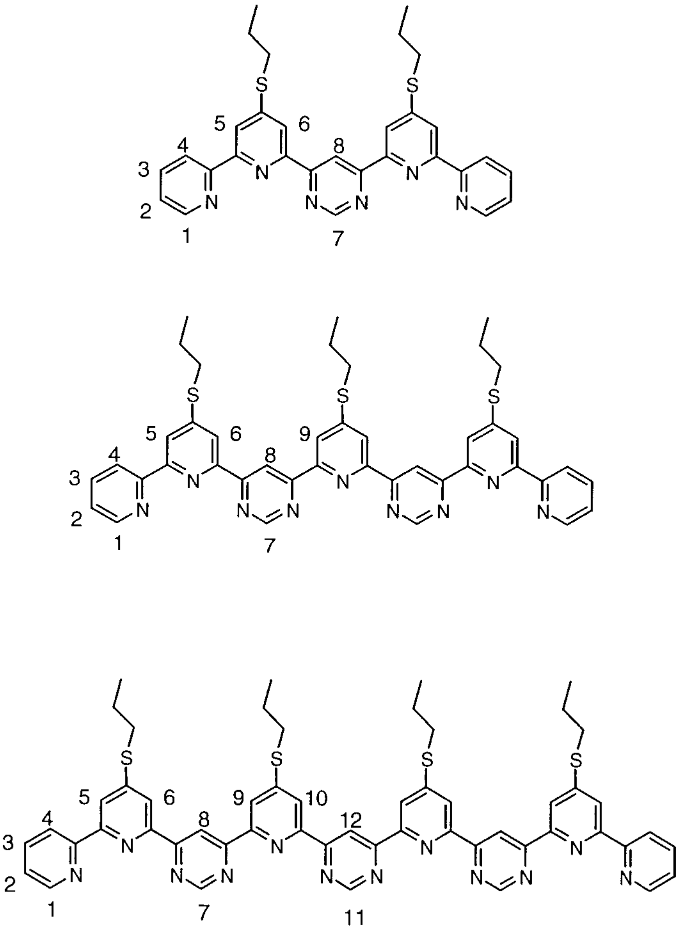
The present results demonstrate the formation of grid-type complexes, based on octahedral coordination sites, from lead(II) ions and tridentate ligand subunits. They confirm the utility of lead(II) ions as a coordination center in self-assembly processes, and open the door to the construction of novel architectures that use heavy metals as assembling sites.[12] The large size of the Pb^{II} ions and the comparatively long bonding distances may allow the generation of novel entities not accessible with transition metal ions. In particular, the [4 × 4]-grid superstructure **4** displays a metal ion array of nanometric size in which the ions are located in a precisely defined fashion, and which gives access to devices based on *ion dots*,[1] reminiscent of the arrays of *quantum dots*, currently investigated as storage media in microelectronics.[13] Such entities represent programmed supramolecular composites of inorganic nature.

The formation of **4** is a very remarkable process that shows again the power of self-assembly for the generation of well-defined inorganic architectures, displaying specific arrays of metal ions. It points to the potential of the supramolecular approach for the spontaneous but controlled assembly of highly complex nanostructures. The application of such an approach to the fabrication of electronic and information storage devices provides means to bypass nanofabrication and nanomanipulation through the designed use of instructed chemical processes.

Experimental Section

Materials: ^{1}H NMR and ROESY measurements were recorded on a 400 MHz Bruker AM400 instrument in CD$_3$CN and CD$_3$NO$_2$, with the use of the residual solvent peak as reference. The *J* values indicated correspond to the observed splittings not to exact coupling constants. ^{207}Pb NMR was performed on a Bruker AC200 instrument at 200 MHz in CD$_3$CN, with Pb(OTf)$_2$ as reference. Lead(II) triflate was prepared from lead(II) oxide and triflic acid by stirring a stoichiometric mixture in H$_2$O at 100 °C for 45 min. The white suspension was filtered and the solvent was removed under low pressure. The salt was purified by diethylether precipitation from a solution in acetonitrile.

General procedure for the formation of the grid-type complexes 2, 3, and 4: An equimolar mixture of Pb(OTf)$_2$ and of ligand **1** in CH$_3$CN was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to yield the final product. The characterization of the complex was performed on this product by means of spectroscopic methods. Elemental analysis gave the correct composition for the product isolated in this way for **2** and **4**, but this is in itself of little help for purity and structure assignment. The numerotations used for the assignment of the ^{1}H NMR signals are given below (Scheme 2).



Scheme 2.

Data for complex 2: Formation from Pb(OTf)$_2$ (28.3 mg); ligand **1b**[6b] (30 mg); CH$_3$CN (5 mL); quantitative yield, see text. ^{1}H NMR (CD$_3$NO$_2$): $\delta = 9.34$ (s, 4H; H7), 9.13 (s, 4H; H8), 8.76 (d, $J = 5.0$ Hz, 8H; H1), 8.63 (s, 8H; H6), 8.43 (d, $J = 8.2$ Hz, 8H; H4), 8.29 (s, 8H; H5), 8.03 (ddd, $J = 8.5$, 7.8, 1.5 Hz, 8H; H3), 7.26 (t, $J = 6.5$ Hz, 8H; H2), 3.36 (t, $J = 7.2$ Hz, 16H), 1.99–1.81 (CH$_3$CN, m, 16H), 1.16 (t, $J = 7.2$ Hz, 24H); assignments made on the basis of the ROESY spectrum; ^{13}C NMR (CD$_3$NO$_2$) $\delta = 15898.0$, 15694.0, 15518.9, 15143.0, 14987.2, 14807.2, 14709.4, 13747.3, 12372.4, 12166.8, 11930.7, 11813.4, 11315.5, 2865.3, 1726.6, 841.5; FAB-MS: *m/z* (%): 4019.3 (20) {[Pb$_4$**1b**$_4$](OTf)$_7$}$^{1+}$, 3870.1 (10) {[Pb$_4$**1b**$_4$](OTf)$_6$}$^{2+}$; C$_{136}$N$_{24}$H$_{112}$S$_{16}$O$_{24}$F$_{24}$Pb$_4$ (4264.25 g mol^{-1}). The same procedure was used for the synthesis of complex **2a**.

Data for complex 3: Formation from: Pb(OTf)$_2$ (20.2 mg); ligand **1c**[6b] (20.5 mg); CH$_3$CN (7 mL); structural characterization, see text. ^{1}H NMR (CD$_3$CN): $\delta = 9.35$ (s, 4H; H7′), 9.04 (s, 8H; H7), 8.95 (s, 4H; H8′), 8.73 (s, 12H; H8, H6′), 8.67 (s, 8H; H6), 8.46 (s, 8H; H9), 8.40–8.25 (m, 12H; H9′, H4), 8.24–8.16 (m, 24H; H5, H4′, H1′, H1), 8.00–7.92 (m, 12H; H3, H5′), 7.85 (t, $J = 7.7$ Hz, 4H; H3′), 7.13 (t, $J = 6.4$ Hz, 12H; H2, H2′), 3.64–3.53 (m, 12H), 3.44–3.36 (m, 24H), 2.13–1.8 (m, 36H), 1.37–1.17 (m, 54H); ES-MS: *m/z* (%): 2139.2 (10) {[Pb$_9$**1c**$_6$](OTf)$_{14}$}$^{4+}$, 1680.4 (12)

$\{[Pb_9$**1c**$_6](OTf)_{13}\}^{5+}$, 1375.8 (22) $\{[Pb_9$**1c**$_6](OTf)_{12}\}^{6+}$ and 1157.6 (15) $\{[Pb_9$**1c**$_6](OTf)_{11}\}^{7+}$; $C_{270}N_{54}H_{234}S_{36}O_{54}F_{54}Pb_9$ (9144.03 g mol^{-1}).

Ligand 1d. This compound was isolated as a side-product in the synthesis of compound **7** in ref. [6b]. The description of the procedure given in ref. [6b] was to be completed as follows: The second yellow band was collected and the solvent removed by rotary evaporation to afford **7** (1.48 g, 2.00 mmol) as yellow powder in 47% yield. The third band was collected and the solvent removed to afford the four-terpyrdine-site ligand (i.e., the present ligand **1d**) as an off-white powder (0.5 g, 0.50 mmol) in 12% yield. ^{1}H NMR ($CDCl_3$) $\delta = 10.20$ (s, 1H; H11), 9.48 (s, 2H; H7), 9.40 (s, 1H; H12), 8.92 (s, 2H; H8), 8.51 (s, 2H), 8.42 (d, $J = 3.9$ Hz, 2H), 8.18 (s, 2H), 8.04 (d, $J = 6.0$ Hz, 2H), 8.02 (s, 2H), 7.83 (s, 2H), 6.85 (dd, $J = 4.5$, 6.1 Hz, 2H), 6.58 (t, $J = 6.3$ Hz, 2H), 3.2 (m, 8H), 1.6–2.0 (m, 8H), 1.18 (m, 12H).

Data for complex 4: Formation from $Pb(OTf)_2$ (39.3 mg); ligand **1d** (38.7 mg); CH_3CN (7 mL); quantitative, see text. ^{1}H NMR (CD_3CN) $\delta =$ 9.34 (s, 4H; H11), 9.18 (s, 4H; H12), 9.08 (s, 4H; H11′), 9.03 (s, 8H; H7), 8.96 (s, 8H; H8), 8.85 (s, 4H; H12′), 8.76 (s, 8H; H10), 8.73 (s, 8H; H7′), 8.67 (s, 8H; H9), 8.62 (s, 8H; H6), 8.54 (s, 8H; H8′), 8.46–8.49 (m, 24H; H1H9′H10′), 8.42 (s, 8H; H6′), 8.39 (d, $J = 7.0$ Hz, 8H; H4′), 8.37 (d, $J = 7.3$ Hz, 8H; H4), 8.16–8.13 (m, 16H; H1′, H5), 7.96 (t, $J = 7.5$ Hz, 8H; H3), 7.91 (t, $J = 7.2$ Hz, 8H; H3′), 7.82 (s, 8H; H5′), 7.17 (t, $J = 6.4$ Hz, 8H; H2), 7.01 (t, $J = 6.4$ Hz, 8H; H2′), 3.65–3.51 (m, 32H), 3.37–3.30 (m, 32H), 2.13–1.8 (m, 64H), 1.32 (t, $J = 7.3$ Hz, 24H), 1.25 (t, $J = 7.3$ Hz, 24H), 1.18, 1.15 (2t, $J = 7.3$ Hz, 48H); ^{207}Pb NMR (reference: $Pb(OTf)_2$): $\delta = 2257.34$ (1), 1857.82 (2), 992.95 (1); ES-MS: m/z (%): 3061.0 (10) $\{[Pb_{16}$**1d**$_8](OTf)_{27}\}^{5+}$, 2525.2 (20) $\{[Pb_{16}$**1d**$_8](OTf)_{26}\}^{6+}$, 2143.3 (50) $\{[Pb_{16}$**1d**$_8](OTf)_{25}\}^{7+}$, 1856.8 (100) $\{[Pb_{16}$**1d**$_8](OTf)_{24}\}^{8+}$, 1634.1 (30) $\{[Pb_{16}$**1d**$_8](OTf)_{23}\}^{9+}$; $C_{464}N_{96}H_{400}S_{64}O_{96}F_{96}Pb_{16}$ (16047.75 g mol^{-1}).

Note: The ^{1}H NMR assignments were made according to the corresponding ROESY spectrum. It is not possible to distinguish between H6 and H9, so in the assignment they could be interchanged. Two sets of signals are found for the two types of ligands; although it is difficult to determine which set is for the inner ligands and the outer ligands, one may expect the signals of the former to be probably more shielded than those of the latter.

X-Ray crystallographic data: The measurements were carried out on a STOE-IPDS diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation. Table 1 summarizes the crystal data, data collection and refinement parameters. All calculations were performed with SHELX-97 package.[14] The structure was solved by direct methods and refined by full-matrix-least-squares based on F^2. All hydrogen atoms, disordered triflates and solvents molecules were refined isotropically. All of the C–H hydrogen atoms were placed in calculated positions with $U(H) = 1.5\,U_{eq}(C)$ for methyl groups and $U(H) = 1.2\,U_{eq}(C)$ for all other. Molecular graphics were generated with SCHAKAL96.[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114942. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data for **2a**.

formula	$C_{96}H_{64}N_{24}Pb_4 \cdot 8\,SO_3CF_3$
M_r [g mol^{-1}]	3575.08
T [K]	200(1)
λ [Å]	0.71073
crystal system	tetragonal
space group	$P\bar{4}2_1c$
a [Å]	15.955(2)
b [Å]	15.955(2)
c [Å]	29.823(6)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	7592(2)
Z	2
ρ_{calcd} [g cm^{-3}]	1.564
μ MoK_α [mm^{-1}]	4.625
$F(000)$	3440
crystal size [mm]	$0.30 \times 0.30 \times 0.20$
Θ [°]	2.26–26.04
index ranges	$-11 \leq h \leq 19$, $-19 \leq k \leq 14$, $-36 \leq l \leq 36$
reflections collected	30170
independent reflections	6998
data/restraints/parameters	6998/302/415
GoF S	1.050
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0589$, $wR_2 = 0.1698$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.1761$
largest diff. peak/hole [e Å^{-3}]	1.681/−1.392

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