[9] a) $3 \cdot 0.5\,C_6H_6$, triclinic, space group $P\bar{1}$, $a = 15.8034(7)$, $b = 21.587(1)$, $c = 22.742(1)$ Å, $\alpha = 94.839(1)$, $\beta = 91.726(1)$, $\gamma = 103.303(1)°$; $V = 7513.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.230\,g\,cm^{-3}$, $\mu = 0.409\,mm^{-1}$, $1.8 < 2\theta < 53.0$. Final R factor was 0.0625 ($wR2 = 0.1514$) for 26531 observed reflections with $I > 2\sigma(I)$. b) $4 \cdot 1.5\,C_6H_6$, triclinic, space group $P\bar{1}$, $a = 14.3308(6)$, $b = 14.8489(9)$, $c = 23.540(1)$ Å, $\beta = 78.816(1)$, $\gamma = 61.248(1)°$; $V = 4190.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.221\,g\,cm^{-3}$, $\mu = 0.387\,mm^{-1}$, $3.22 < 2\theta < 52.90$. Final R factor was 0.0585 ($wR2 = 0.1413$) for 4066 observed reflections with $I > 2\sigma(I)$. c) $5 \cdot C_6H_6$, triclinic, space group $P\bar{1}$, $a = 11.0417(5)$, $b = 14.3909(7)$, $c = 22.445(1)$ Å, $\alpha = 92.955(1)$, $\beta = 98.253(1)$, $\gamma = 107.244(1)°$; $V = 3354.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.274\,g\,cm^{-3}$, $\mu = 0.429\,mm^{-1}$, $1.8 < 2\theta < 46.6$. Final R factor was 0.0524 ($wR2 = 0.1379$) for 9003 observed reflections with $I > 2\sigma(I)$. d) $6 \cdot CH_3CN \cdot 2\,C_6H_6$, orthorhombic, space group $Pnma$, $a = 21.838(1)$, $b = 31.824(2)$, $c = 17.1990(8)$ Å; $V = 11953(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.264\,g\,cm^{-3}$, $\mu = 0.449\,mm^{-1}$, $2.6 < 2\theta < 53.0$. Final R factor was 0.1249 ($wR2 = 0.3333$) for 12087 observed reflections with $I > 2\sigma(I)$.

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A Graphite-Like Complex with Large Cavities Constructed with the Complex Ligand [Ni^{II}(bpca)$_2$]**

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Recently metal complex assemblages have attracted much attention and several examples have been reported, including multiple helicates,[1] grids,[2] cages,[3] two-dimensional sheets,[4–6a, b] diamondoid networks,[7] and zeolite mimics.[8] In

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such compounds cooperative interactions between the metal ions often induce properties such as magnetism,[4–6b–h] conductivity,[9] and photoactivity.[6f–h] It has been shown that the use of a "complex ligand" as a building component is effective not only in the construction of the desired structures but also to design the spatial arrangement of metal ions, and to tune the metal – metal interactions. We have developed a strategy for constructing trinuclear and chain complexes by using [M(bpca)$_2$]$^{n+}$ as bis-bidentate complex ligands (where $n = 1$ for M = Fe^{III}; $n = 0$ for M = Mn^{II} and Fe^{II}; Hbpca = bis(2-pyridylcarbonyl)amine).[10] Herein, we report the synthesis and structure of a two-dimensional coordination polymer constructed by the reaction of [Ni(bpca)$_2$] (**1**) with iron(II) perchlorate (Scheme 1).
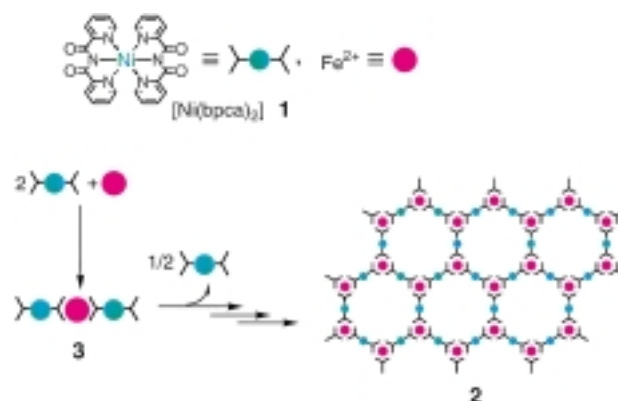
Scheme 1. Schematic representation for the formation of the honeycomb complex **2** by the reaction of **1** with iron(II) ion.

The reaction of **1** with iron(II) perchlorate hexahydrate in a 2:1 molar ratio afforded dark purple hexagonal prismatic crystals of [Fe^{II}(**1**)$_{1.5}$](ClO$_4$)$_2$ (**2**), a compound with a two-dimensional structure. Addition of one drop of water to the same reaction mixture afforded different deep violet crystals of the trinuclear species [Fe^{II}(**1**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (**3**) which is considered to be a precursor of **2**.

Figure 1 shows the two-dimensional honeycomb structure of **2**. The structure is that of a (6,3) net[11] in which the triply chelated iron(II) centers act as three-connected nodes (Figure 1a). Each ring in a layer consists of six iron(II) ions at the corners and six units of **1** as the edges. The diagonal separations are Fe1#2 ··· Fe1#3 = 16.463(3) Å and Ni1 ··· Ni1#1 = 21.582(1) Å. The cavity size estimated from the space-filling model (Figure 1b) is 12 Å along the Fe1#2 ··· Fe1#3 axis and 13 Å along the Ni1 ··· Ni1#1 axis. The whole structure of **2** is made up, as in graphite, of layers stacked upon each other along the c axis and related by crystallographical mirror planes at $c = 0$ and 0.5, hence the complete channel is formed along the c axis. The iron(II) centers are in a chiral environment formed by three chelating complex ligands, and a single layer consists of only one of the two optical isomers (Λ or Δ). It is to be noted that **2** has noninterpenetrating networks regardless of the presence of the large cavities.[4, 11] Interpenetration is prevented by the steric repulsion of the pyridine rings of the complex ligands. The perchlorate ions are located between the layers, half of them form two alternate
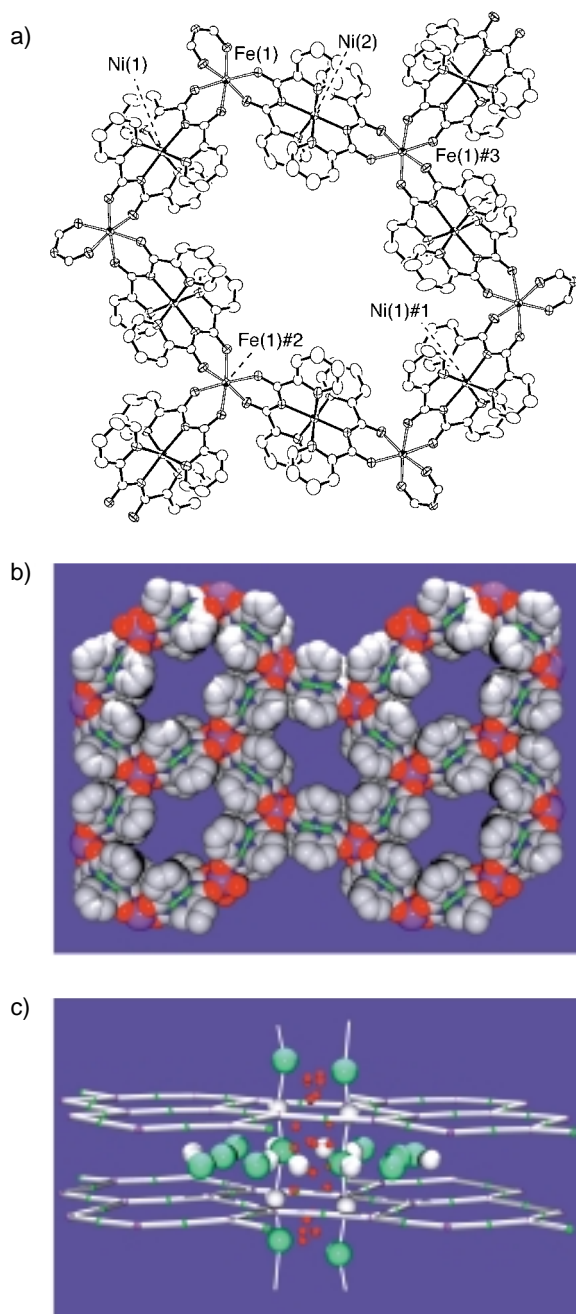
Figure 1. a) ORTEP drawing of **2** with the thermal ellipsoids set at 50 % probability. b) Space-filling drawing of **2**. The hydrogen atoms are omitted. c) Schematic drawing of the counter ions and solvent molecules in **2**. Green: ClO_4^-, white: $CHCl_3$, and red: H_2O, relevant distances [Å]: Ni(1)-N(pyridine) 2.087(5) – 2.114(5), Ni(1)-N(amide) 2.013(5) – 2.020(5), Ni(1)-Fe(1) 5.4238(11), Ni(2)-Fe(1) 5.3859(8), Fe(1)-O 2.072(4) – 2.109(4); symmetry codes: (#1) $-x+1, -y+1, z$; (#2) $x, y-1, z$; (#3) $-x+1, -y+2, z$.

one-dimensional arrays with chloroform molecules along the c axis which penetrate the channel (Figure 1 c). More than ten water molecules were found within each ring. Compound **2** undergoes anion exchange and also exchange of the solvent molecules of crystallization in the solid state without the disintegration of the honeycomb structure.[12]

Figure 2 shows an ORTEP plot of the complex ion in the trinuclear complex **3**. This compound consists of two [Ni^{II}-

(bpca)$_2$] units (shown with filled-in bonds) and a central [Fe^{II}(H$_2$O)$_2$]$^{2+}$ ion (shown with open bonds), the former act as terminal ligands to the central iron(II) ion. The overall

Figure 2. ORTEP plot of the cation of **3** with the thermal ellipsoids set at 50 % probability. Selected distances [Å]: Ni1-N5 2.006(3), Ni1-N2 2.037(3), Ni1-N4 2.081(4), Ni1-N6 2.087(4), Ni1-N3 2.120(4), Ni1-N1 2.122(4), Ni1-Fe1 5.3681(5), Fe1-O1 2.020(3), Fe1-O2 2.065(3), Fe1-O5 2.104(6); symmetry codes: (#1) $-x, -y, -z$.

structure of the cationic part of **3** is similar to that of the mixed valent iron trinuclear complex [Fe^{II}{Fe^{III}(bpca)$_2$}$_2$(H$_2$O)$_2$]$^{4+}$ we reported previously.[10b] The hexacoordination of the iron(II) ion in **3** is by four carbonyl oxygen atoms from **1** and by two additional oxygen atoms from the water molecules bound *trans* to each other.
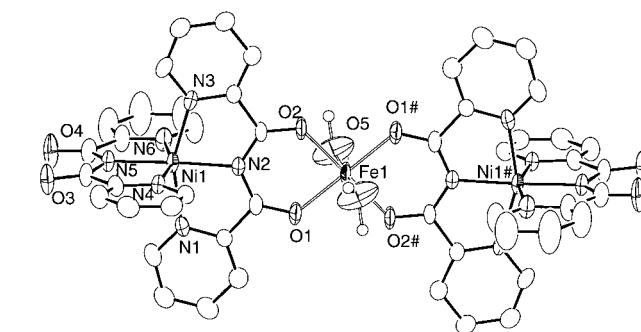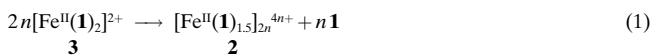
We found that the best conditions for the synthesis of the honeycomb complex **2** are the reaction of **1** and iron(II) perchlorate in a 2:1 ratio under the water free conditions. The reaction in a 3:2 ratio gave a mixture of **2** and a one-dimensional chain complex **4**[13] even though the reaction ratio is consistent with the component ratio in **2**. To investigate the formation mechanism of **2**, we carried out an ESI-mass spectrometric study of the reaction solution of **1** and iron(II) perchlorate. The main product in a 2:1 solution was a trinuclear complex with a "doubly chelated" iron center formulated as [Fe(**1**)$_2$(ClO$_4$)]$^+$ (m/z: 1176.98), and a tetra-nuclear complex with a "triply chelated" iron center, formulated as [Fe(**1**)$_3$(ClO$_4$)]$^+$ (m/z: 1687.08), was found as a trace product. A similar result was obtained for a 3:1 solution, a triply chelated species in which three units of **1** are coordinated to the central iron(II) ion was a minor product even under these conditions. These results indicate that the precursor for the honeycomb complex **2** is the trinuclear complex **3** with a doubly chelated iron center and not [Fe(**1**)$_3$]$^{2+}$ with a triply chelated iron center. Complex **3** has four coordination-free carbonyl sites (O3 and O4 in Figure 2) and thereby acts as a trinuclear complex ligand. The total reaction for the formation of the honeycomb complex **2** is expressed in [Eq. (1)].

$$2n[Fe^{II}(\mathbf{1})_2]^{2+} \longrightarrow [Fe^{II}(\mathbf{1})_{1.5}]_{2n}^{4n+} + n\,\mathbf{1} \qquad (1)$$
$$\phantom{2n[Fe^{II}(\mathbf{1})_2]^{2+}} \mathbf{3} \mathbf{2}$$

The fact that the 3:2 reaction gave a mixture of **2** and **4** may be understood in the following way. Under these conditions, the reaction in [Eq. (1)] gives **2**; but since free iron(II) ions are present in larger amounts than in the 2:1 reaction, the reaction in [Eq. (2)] occurs at the same time to produce the chain

$$[Fe^{II}(\mathbf{1})_2]^{2+} + Fe^{II} \longrightarrow \mathbf{4} \qquad (2)$$

complex **4**, which, because of its low solubility is formed as a solid product. The reaction in [Eq. (1)] does not proceed when the reaction medium is wet (see above). The presence of an excess of water molecules appears to stabilize **3** and prevent the formation of **2**.

In conclusion, we have prepared the graphite-like compound **2**, which has large cavities and no interpenetration, the related discrete trinuclear and one-dimensional complexes were also prepared. Formation of these complexes depends on the reaction stoichiometry and the presence or the absence of water.

Experimental Section

Mass spectra (ESI) were recorded on a JASCO API LC-TOF/MS instrument.

2·4.5 CHCl$_3$·3 MeOH·10 H$_2$O: Chloroform was distilled before use to remove ethanol. A solution of [Fe(H$_2$O)$_6$](ClO$_4$)$_2$ in methanol (0.025 M; 0.01 mmol, 0.4 mL) was added to a solution of [Ni(bpca)$_2$] (10 mg, 0.02 mmol) in chloroform/methanol (1/1 (v/v), 2 mL). Slow evaporation of the solvent at room temperature gave black hexagonal prisms of **2**·4.5 CHCl$_3$·3 MeOH·10 H$_2$O which were filtered and dried in vacuo (11 mg).

3·4 H$_2$O: A solution of [Fe(H$_2$O)$_6$](ClO$_4$)$_2$ in methanol (0.02 M; 0.01 mmol, 0.5 mL) was added to a solution of [Ni(bpca)$_2$] (10 mg, 0.02 mmol) in chloroform/methanol (1/1 (v/v), 2 mL). A drop of water was added to the resulting dark purple solution. Slow evaporation of the solvent at room temperature gave black plates of **3**·4 H$_2$O (almost quantitatively (13 mg).

Crystal-structure determinations: Bruker SMART-1000 CCD-based diffractometer, 200 K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). **2**·4.5 CHCl$_3$·3 MeOH·10 H$_2$O: Orthorhombic, space group $Pnnm$, $a = 32.999(2)$, $b = 17.1473(13)$, $c = 20.9802(13)$ Å, $V = 11871.4(13)$ Å^3, $\rho_{calcd} = 1.598$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 1.186$ mm^{-1}; ω-scans, 76878 reflections measured ($2\theta_{max} = 55°$), of which 14045 were independent and 7052 were observed [$I > 2\sigma(I)$], 792 refined parameters, $R = 0.0873$, $wR2 = 0.2532$, residual electron density max./min. 1.675/ − 0.943 e Å^{-3}. Ten peaks were found after D-Fourier peak search, and were assigned as water molecules. **3**·4 H$_2$O. Triclinic, space group $P\bar{1}$, $a = 8.9267(6)$, $b = 12.2683(8)$, $c = 13.3292(9)$ Å, $\alpha = 90.215(2)$, $\beta = 101.813(2)$, $\gamma = 97.288(2)°$, $V = 1416.63(16)$ Å^3, $\rho_{calcd} = 1.624$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 1.095$ mm^{-1}; ω scans, 10168 reflections measured ($2\theta_{max} = 55°$), of which 6288 were independent and 3635 were observed [$I > 2\sigma(I)$], 394 refined parameters, $R = 0.0598$, $wR2 = 0.1323$, residual electron density max./min. 0.807/ − 0.589 e Å^{-3}. The structures were solved by the direct method with SHELXS-86[14] or the Patterson method with DIRDIF94 (Patty),[15] and refined by the least squares method on F^2, SHELXL-93.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated by the geometrical method and refined as a riding model. 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-141630 and CCDC-141631. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] In **2**, ClO$_4^-$ ions can be exchanged with PF$_6^-$ ions in the solid state, and CHCl$_3$ molecules can be exchanged with CHBr$_3$ molecules. These facts are comfirmed by IR spectra and by the specific gravity.

[13] Compound **4** is a one-dimensional alternate chain complex which consists of the bridging **1** and [Fe(EtOH)$_2$]$^{2+}$ units. The iron(II) ion in this complex is coordinated by two complex ligands and two EtOH molecules. The latter comes from the stabilizer in CHCl$_3$. Crystal data of **4**: Monoclinic, space group $C2/c$, $a = 10.4651(5)$, $b = 18.6142(10)$, $c = 20.3093(11)$ Å, $\beta = 102.8680(10)°$, $V = 3856.9(3)$ Å^3, $Z = 4$, $R = 0.0435$, $wR2 = 0.1239$ [$I > 2\sigma(I)$].

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