

# Second-Sphere Coordination of the Tris(5,5'-diamino-2,2'-bipyridine)iron Complex With Arene-Carboxylate Ligands Through N-H···O Hydrogen Bonding

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**Abstract.** The tris(5,5'-diamino-2,2'-bipyridine)iron(II) complex  $[Fe(DABP)_3]^{2+}$  can be engaged in hydrogen-bonding interactions from the amino groups to carboxylate-containing molecules as H-bond acceptors. This so-called second-sphere coordination of the metal complex is investigated here by using benzene-1,4-dicarboxylate (terephthalate,  $L^1$ ), benzene-1,3-dicarboxylate (isophthalate,  $L^2$ ), biphenyl-2,2'-dicarboxylate ( $L^3$ ), and benzene-1,3,5-tricarboxylate (trimesate,  $L^4$ ) anions for N-H···O bonding. The second-sphere coordination of  $[Fe(DABP)_3]^{2+}$  is further complemented by water molecules of crystallization in the isolated and structurally elucidated compounds of  $[Fe(DABP)_3](L^1)\cdot 5H_2O$ ,  $[Fe(DABP)_3](L^2)\cdot 8H_2O$ ,  $[Fe(DABP)_3](L^3)\cdot 12.5H_2O$ , and

$[Fe(DABP)_3](L^4)\cdot 20H_2O$ . The hydrogen-bonding between  $[Fe(DABP)_3]^{2+}$  and the dicarboxylate anions ( $L^1-L^3$ ) decreases from a three-dimensional supramolecular network (with  $L^1$ ) to discrete units (with  $L^2$  and  $L^3$ ) with the increasing number of crystal water molecules. The tricarboxylate ligand  $L^4$  is capable of capping the triangular face formed by the three amino groups in  $[Fe(DABP)_3]^{2+}$ . The solid-state structures of DABP·2H<sub>2</sub>O and 5,5'-bis(ethoxycarbonylamino)-2,2'-bipyridine (BEBP) are reported.

**Keywords:** Second-sphere coordination; Supramolecular chemistry; Hydrogen bonding; Bipyridine complexes; Iron complex

## Die zweite Koordinationssphäre des Tris(5,5'-diamino-2,2'-bipyridin)eisen-Komplexes mit Aren-Carboxylat-Liganden über N-H···O Wasserstoff-Bindungen

**Inhaltsübersicht.** Der Tris(5,5'-diamino-2,2'-bipyridin)eisen(II)-Komplex  $[Fe(DABP)_3]^{2+}$  kann Wasserstoff-Brücken von den Amino-Gruppen zu Carboxylat-haltigen Molekülen als H-Akzeptoren ausbilden. Diese so genannte zweite Koordinationssphäre des Metall-Komplexes wird hier unter Verwendung von Benzol-1,4-dicarboxylat (Terephthalat,  $L^1$ ), Benzol-1,3-dicarboxylat (Isophthalat,  $L^2$ ), Biphenyl-2,2'-dicarboxylat ( $L^3$ ) und Benzol-1,3,5-tricarboxylat (Trimesat,  $L^4$ ) als Anionen für N-H···O Bindungen untersucht. Die zweite Koordinationssphäre von  $[Fe(DABP)_3]^{2+}$  wird weiterhin von Kristallwasser-Molekülen in den isolierten und strukturell charakterisierten Verbindungen  $[Fe(DABP)_3](L^1)\cdot 5H_2O$ ,

$[Fe(DABP)_3](L^2)\cdot 8H_2O$ ,  $[Fe(DABP)_3](L^3)\cdot 12.5H_2O$ , and  $[Fe(DABP)_3](L^4)\cdot 20H_2O$  vervollständigt. Die Wasserstoff-Brückenbindungen zwischen  $[Fe(DABP)_3]^{2+}$  und den Dicarboxylat-Anionen ( $L^1-L^3$ ) nehmen von einem dreidimensionalen supramolekularen Netzwerk (mit  $L^1$ ) zu diskreten Einheiten (mit  $L^2$  und  $L^3$ ) hin mit steigender Zahl von Kristallwasser-Molekülen ab. Der Tricarboxylat-Ligand  $L^4$  vermag die von drei Amino-Gruppen in  $[Fe(DABP)_3]^{2+}$  gebildete Dreiecksfläche zu überdachen. Die Festkörperstrukturen von DABP·2H<sub>2</sub>O und 5,5'-Bis(ethoxycarbonyl-amino)-2,2'-bipyridin (BEBP) werden beschrieben.

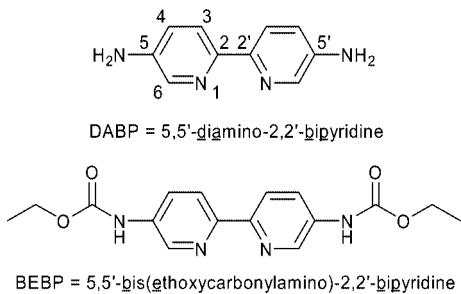
## Introduction

The field of crystal engineering is of growing interest and numerous work has been done on the assembly of supramolecular systems such as host-guest recognition, inclusion and encapsulation [1, 2]. Many efforts in this field have focused on the predictable assembly of organic molecular solids and metal coordination compounds (coordination polymers) [3, 4, 5, 6]. Metal complexes allow for the pre-

orientation of the building blocks according to the metal coordination geometry [7]. One of the strategies for the construction of such supramolecular architectures is by second-sphere coordination – the interaction between already coordinatively saturated metal complexes and external ligands, e.g. through hydrogen bonding [8, 9]. A variety of biochemical systems utilize second-sphere coordination for the modification of the chemistry around metal ions [10, 11]. In order to enable supramolecular second coordination-sphere systems, some functional groups must be appended to the first-sphere ligand. These groups should not coordinate to a metal center in the formation of the first-sphere complex, but bind the external ligands (that is the second-sphere ligands) to build supramolecular systems. The ligand 5,5'-diamino-2,2'-bipyridine (DABP) [12, 13] and derivatives such as 5,5'-bis(ethoxycarbonylamino)-2,2'-

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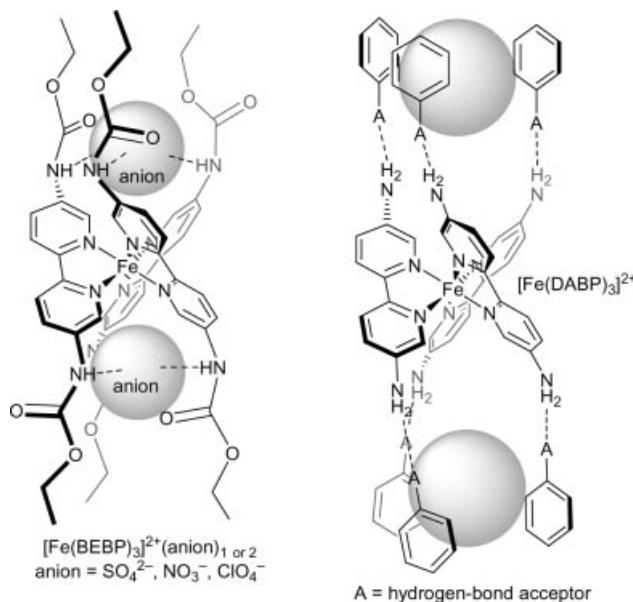
bipyridine (BEBP) [14, 15] possess the dual functions. Only the bipyridine nitrogen atoms but not the amino groups were, so far, found capable of coordinating to a metal ion, yielding the primary complex, e.g.  $[M(DABP)_3]^{2+}$ . This complex can then serve as a building block for larger supramolecular assemblies because the free amino groups are good hydrogen bond donors.



The amino groups of the metal-bound DABP ligand have been found to enter into N-H $\cdots$ O hydrogen bonding to water molecules of crystallization or in N-H $\cdots$ X hydrogen bonding to anions ( $X = SCN^-$ ,  $SO_4^{2-}$ ,  $Cl^-$ ) or acceptor ligands in  $M(DABP)_yX_2$  moieties ( $X = Cl$ ,  $N_3$ ) [12]. The second-sphere coordination of  $[M(DABP)_3]^{2+}$  complexes with crown ethers led to the supramolecular assemblies of  $\{[Ni(DABP)_3]\cdot(18-C-6)\}Cl_2\cdot4CH_3OH$  (kinked 2<sub>1</sub>-helical chain) and  $\{[Zn(DABP)_3]\cdot(18-C-6)\}(NO_3)_2\cdot3/8H_2O$  (linear strands) [13]. The first-sphere complexes with 5,5'-disubstituted-2,2'-bipyridine ligands have a favorable pre-organized conformation such that the substituents on the 5-position form clefts which may encapsulate other species. For instance, three BEBP and similar 5,5'-disubstituted-2,2'-bipyridine ligands around a metal atom form two clefts which can encapsulate anions (Scheme 1, left) [14, 16]. Meanwhile, the orientation of the six amino groups in complexes  $[M(DABP)_3]^{2+}$  should allow for the extension of the two triangular clefts, for example, by attaching hydrogen-bond acceptor groups, as visualized in Scheme 1, right.

We have recently communicated the supramolecular compound  $Fe^3(DABP)_3^{2+}[Fe^2(DABP)_3]^{2-}Fe^1(DABP)_3(nitrophenolate)_6]^{2-}$  where six nitrophenolate H-bond acceptors create a cavity which is filled through self-inclusion [17] of a crystallographically independent  $[Fe(DABP)_3]^{2+}$ -cation (Scheme 2) [18].

Here we continue our design of such clefts or cavities with the second-sphere hydrogen-bonding coordination of carboxylate anions to the  $[Fe(DABP)_3]^{2+}$  cation. The aromatic polycarboxylate anions should function as H-bond acceptors from the amino groups and thereby form funnel-shaped openings (see Scheme 1). The use of divalent anions may lead to extended supramolecular, hydrogen-bonded networks. Polycarboxylates are among the most useful and versatile compounds for the formation of supramolecular architectures [4, 19, 20]. We report the solid state structures of the two ligands DABP $\cdot$ 2H<sub>2</sub>O and BEBP and of four second-sphere complexes formed from  $[Fe(DABP)_3]^{2+}$  with the anions of benzene-1,4-dicarboxylate (terephthalate,



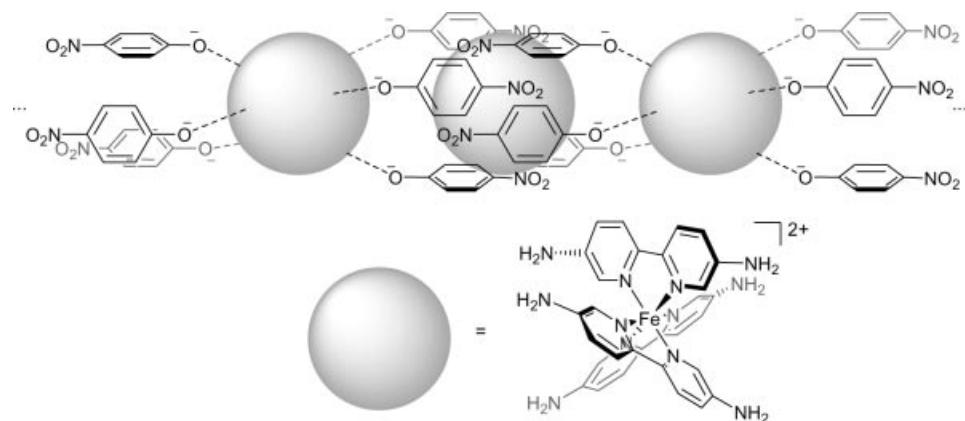
Scheme 1 Schematic presentation of the cleft formation in metal complexes with three 5,5'-disubstituted-2,2'-bipyridine ligands.

( $L^1$ ) $^{2-}$ ), benzene-1,3-dicarboxylate (isophthalate, ( $L^2$ ) $^{2-}$ ), biphenyl-2,2'-dicarboxylate, ( $L^3$ ) $^{2-}$ , and benzene-1,3,5-tricarboxylate, ( $L^4$ ) $^{3-}$  through N-H $\cdots$ O hydrogen bonding. The structure of compound 6,  $\{[Fe(DABP)_3](L^4)_2\}\cdot20H_2O$  has been briefly communicated before [13].

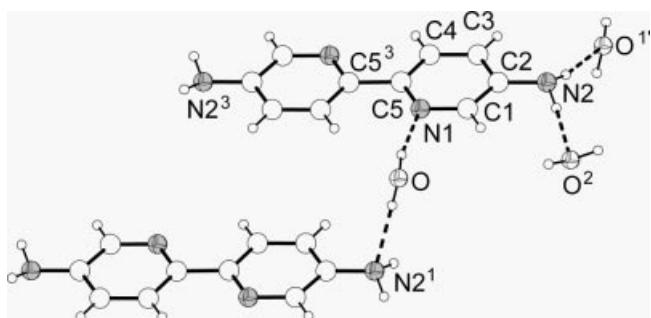
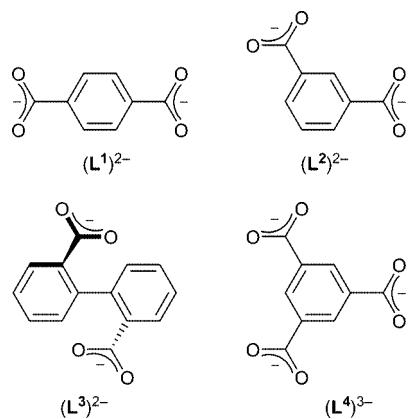
## Results and Discussion

The crystal structures of the BEBP (**1**) and DABP (**2**) ligands reveal the hydrogen-bonding donor character of the amino groups (Fig. 1 and 2). The amino group in **2** can also function as a hydrogen-bond acceptor. It is noteworthy that the amino group in metal complexes of **2** has, so far, never been observed as a donor towards metal atoms. Although structural studies of DABP-metal complexes where the amino-hydrogen atoms could be found and refined showed seldom coplanarity of the amino group with the aromatic ring but often a pyramidalization at the amino N-atom even without the function of an H-acceptor (Table 2) [12, 15, 18]. The pyridyl groups in both ligands assume the *s-trans* form as the preferred conformation [21].

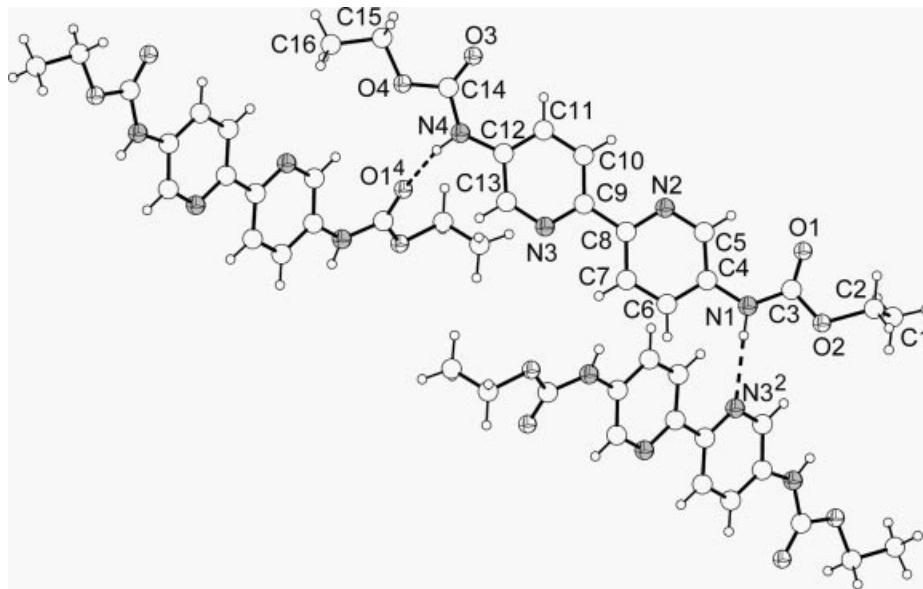
Following our results from the second-sphere coordination of  $[Fe(DABP)_3]^{2+}$  with *p*-nitrophenolate [18] and crown ethers [13] it was expected that arene-di- or -tricarboxylate anions might act as a connector for the metal-complexes through hydrogen-bonding from the NH<sub>2</sub> to the COO<sup>-</sup> groups. The supramolecular  $[Fe(DABP)_3]^{2+}$ -carboxylate adducts could be obtained by reaction of  $[Fe(DABP)_3]SO_4$  with the disodium salt of benzene-1,4-dicarboxylate (terephthalate, ( $L^1$ ) $^{2-}$ ) or by intermediate formation of  $[Fe(DABP)_3](OH)_2$  through salt elimination with Ba(OH)<sub>2</sub> ( $\rightarrow BaSO_4 \downarrow$ ) followed by reaction with benzene-1,3-dicarboxylic acid (isophthalic acid, H<sub>2</sub> $L^2$ ), biphenyl-2,2'-dicarboxylic acid (H<sub>2</sub> $L^3$ ) or benzene-1,3,5-tricarboxylic



**Scheme 2** Schematic presentation of the self host-guest system [17] in  $\text{Fe}^3(\text{DABP})_3^{2+}[\text{Fe}^2(\text{DABP})_3 \subset \text{Fe}^1(\text{DABP})_3(\text{nitrophenolate})_6]^{2-}$  [18].



**Fig. 2** Section of the packing diagram of DABP·2H<sub>2</sub>O (**2**), showing the hydrogen-bonding interactions; see Table 1 for details; additional symmetry transformation: <sup>3</sup> = -x+1, -y+1, z.



**Fig. 1** Section of the packing diagram of BEBP (**1**), showing the hydrogen-bonding interactions; see Table 1 for details.

acid (trimesic acid,  $\text{H}_3\text{L}^4$ ). The preset  $[\text{Fe}(\text{DABP})_3]^{2+}$ : carboxylate-ligand reactant ratio of 1:1 for the dicarboxylates  $(\text{L}^1)^{2-}$  to  $(\text{L}^3)^{2-}$  was also observed in the final products of formula  $[\text{Fe}(\text{DABP})_3](\text{L}^{1-3})$  that is the dicarboxylate was the

only anion in these supramolecular structures. For the trimesic acid ( $\text{L}^4)^{3-}$  the reactant ratio was chosen as 3:2 to reach neutrality in the anticipated product of formula  $[\text{Fe}(\text{DABP})_3]_3(\text{L}^4)_2$ . Crystals were grown in water and in all

**Table 1** Selected hydrogen-bonding interactions involving the amino groups in **1–6**.<sup>a)</sup>

D-H···A	D-H Å	H···A Å	D···A Å	D-H···A °	symm. transformat. of labelled atom
BEBP, <b>1</b>					
N1-H1A···N3 <sup>2</sup>	0.88(3)	2.10(3)	2.976(3)	171(2)	-x+3/2, y+1/2, -z+1/2
N4-H4A···O1 <sup>4</sup>	0.90(3)	2.05(3)	2.887(3)	154(2)	x-1/2, -y+1/2, z-1/2
DABP·2H <sub>2</sub> O, <b>2</b>					
N2-H2A···O <sup>2</sup>	0.92(2)	2.15(2)	3.060(2)	169(2)	-x+1, y+1/2, -z+1/2
N2-H2B···O1'	0.92(2)	2.06(2)	2.976(2)	170(2)	x+1, y+1, z
O-H0B···N2 <sup>1</sup>	0.92(2)	2.04(2)	2.950(2)	169(2)	x, y-1, z
O-H0A···N1	0.93(2)	1.91(2)	2.822(2)	168(2)	
[Fe(DABP) <sub>3</sub> (L <sup>1</sup> )·5H <sub>2</sub> O, <b>3</b>					
N4 <sup>2</sup> -H4B···O4	0.81(3)	2.17(3)	2.930(3)	156(3)	-x, y-1/2, -z-3/2
N6-H6A···O1 <sup>3</sup>	0.89(3)	2.11(3)	2.988(3)	172(3)	-x+1, -y+1, -z-1
N6 <sup>4</sup> -H6B···O1 <sup>3</sup>	0.88(3)	2.16(3)	3.021(3)	165(3)	x, -y+3/2, z-1/2 / -x+1, -y+1, -z-1
N8 <sup>3</sup> -H8B···O3	0.86(3)	2.35(3)	3.144(4)	154(3)	-x, -y+1, -z
[Fe(DABP) <sub>3</sub> (L <sup>2</sup> )·8H <sub>2</sub> O, <b>4</b>					
N2-H2A···O1 <sup>3</sup>	0.86	2.22	3.075(6)	175	x-1/2, y+1/2, z
N8-H8B···O1 <sup>7</sup>	0.86	2.00	2.830(6)	162	-x-3/2, -y-5/2, -z-1
[Fe(DABP) <sub>3</sub> (L <sup>3</sup> )·12.5H <sub>2</sub> O, <b>5</b>					
N6-H6A···O2 <sup>2 b)</sup>	0.87	2.54	3.229(5)	137	-x-1/2, y-1/2, -z+3/2
N16-H16A···O8 <sup>4 b)</sup>	0.87	2.12	2.958(5)	161	x-1/2, -y+3/2, z+1/2
[Fe(DABP) <sub>3</sub> (L <sup>4</sup> ) <sub>2</sub> ·20H <sub>2</sub> O, <b>6</b>					
(Fe1-)N3-H3A···O3 <sup>4</sup>	0.870	2.06	2.90(2)	162	y+1/2, x-1/2, z+1/2
(Fe1-)N4-H4A···O2 <sup>3</sup>	0.870	2.25	2.95(2)	137	y, z, x+1
(Fe3-)N11-H11B···O3 <sup>2</sup>	0.870	2.23	3.00(2)	148	z+1, x, y

<sup>a)</sup> D = Donor, A = Acceptor. Only hydrogen bonds between [Fe(DABP)<sub>3</sub>]<sup>2+</sup> and L are listed for the adducts **3–6**. Hydrogen bonds involving water of crystallization are not included here. Hydrogen bonds between the amino groups and water molecules are collected in the deposited cif-files. For found and refined atoms the standard deviations are given. – <sup>b)</sup> Two independent molecules in the unit cell.

**Table 2** Acute interplanar angle between the NH<sub>2</sub>-group and its pyridyl ring in (metal-)DABP structures.<sup>a)</sup>

Compound	Acute interplanar angle/ <sup>o</sup> <sup>b)</sup>	NH <sub>2</sub> -group also H-bond acceptor	Ref.
DABP·2H <sub>2</sub> O, <b>1</b>	37(2)	yes, O-H···N	This work
[CuCl <sub>2</sub> (DABP)]	9(4)	no	[12]
[Ni(DABP) <sub>3</sub> (SCN) <sub>2</sub>	7(3), 9(3), 19(3), 23(3), 27(3), 46(2) <sup>c)</sup>	no	[12]
<sup>1</sup> / <sub>2</sub> [Cu(μ-SO <sub>4</sub> )(DABP)(H <sub>2</sub> O)] <sub>2</sub> ·3H <sub>2</sub> O	47(3), 51(3) <sup>c)</sup>	yes, O-H···N	[12]
[Mn(N <sub>3</sub> ) <sub>2</sub> (DABP) <sub>2</sub> ]	25(2), 31(2) <sup>c)</sup>	no	[12]
[Ru(2,2'-bipy) <sub>2</sub> (DABP)][PF <sub>6</sub> ] <sub>2</sub> ·2CH <sub>3</sub> OH	37(9), 49(8) <sup>c)</sup>	no	[15]
[Fe(DABP) <sub>3</sub> ] <sup>-</sup>	33(3), 37(3) <sup>c)</sup>	yes, N-H···N	[18]
[Fe(DABP) <sub>3</sub> ] <sup>-</sup> ·[Fe(DABP) <sub>3</sub> (nitrophenolate) <sub>6</sub> ] <sup>-</sup>	25(3), 30(3), 36(3), 46(3) <sup>c)</sup>	yes, N-H···N	[18]
[Fe(DABP) <sub>3</sub> ](L <sup>1</sup> )·5H <sub>2</sub> O, <b>3</b>	6(3), 9(3), 10(3), 14(3), 27(3), 48(3) <sup>c)</sup>	no	This work
		yes, O-H···N	

<sup>a)</sup> Only compounds where the the amino-hydrogen atoms could be found and refined. – <sup>b)</sup> Calculated with the program PLATON for Windows [22] by specifying the NH<sub>2</sub>-group(s) as (an) additional plane(s) (lsp1 Nx Hx1 Hx2). An ideal pyramidalization at the nitrogen atom with angles of 107° at N would correspond to an interplanar angle of 61°. An angle of 0° would indicate coplanarity of NH<sub>2</sub> with the pyridyl ring. – <sup>c)</sup> Angle for each different NH<sub>2</sub> group listed separately.

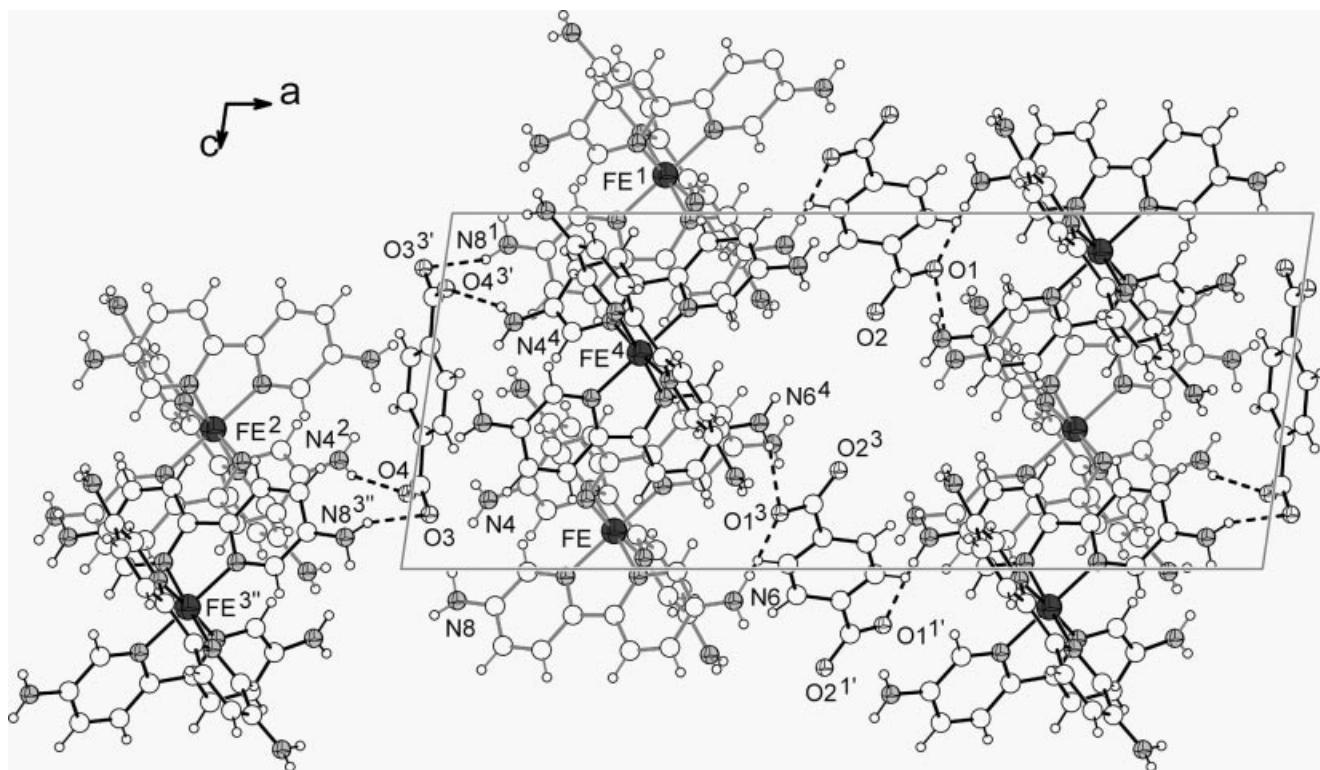
products water molecules of crystallization complement the crystal packing.

The pseudo-octahedral tris(chelate)-metal environment in the first-sphere complexes [Fe(DABP)<sub>3</sub>]<sup>2+</sup> in compounds **3–6** is typical and will not be detailed any further here but has been described in the parent compound [Fe(DABP)<sub>3</sub>]SO<sub>4</sub> and in other [Fe(bipy)<sub>3</sub>]<sup>2+</sup> complexes (bipy = 2,2'-bipyridine) [12, 13, 23, 24, 25, 26]. In the following structural discussions we will focus mostly on the [Fe(DABP)<sub>3</sub>]<sup>2+</sup>-carboxylate interactions and packing, thereby also leaving aside the hydrogen bonding to and from the crystal water.

The benzene-1,4-dicarboxylate adduct [Fe(DABP)<sub>3</sub>](L<sup>1</sup>)·5H<sub>2</sub>O (**3**) crystallizes with a three-dimensional supramol-

ecular structure, formed by two crystallographically different types of L<sup>1</sup> connectors (Fig. 3). The asymmetric unit contains one [Fe(DABP)<sub>3</sub>]<sup>2+</sup> cation, two hemi-L<sup>1</sup> anions, each with one carboxylate group and half of a benzene ring, and five H<sub>2</sub>O molecules. One L<sup>1</sup> connector (with O3,O4) links four [Fe(DABP)<sub>3</sub>]<sup>2+</sup> units by four hydrogen bonds from -NH<sub>2</sub> to -COO<sup>-</sup> groups. The other L<sup>1</sup> connector (the one with O1,O2) links three metal units. The packing in **3** can be described in terms of separated layers of [Fe(DABP)<sub>3</sub>]<sup>2+</sup> or L<sup>1</sup> units parallel to the bc plane which alternate along the a direction (see Fig. 3).

In the benzene-1,3-dicarboxylate adduct [Fe(DABP)<sub>3</sub>](L<sup>2</sup>)·8H<sub>2</sub>O (**4**) there are only two unique hydrogen bonds



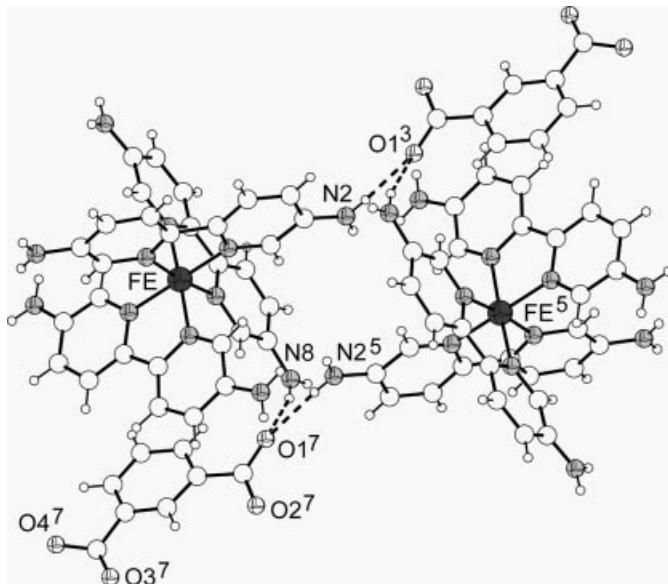
**Fig. 3** Packing diagram of  $[\text{Fe}(\text{DABP})_3](\text{L}^1)$  in **3** showing the hydrogen-bonding interactions (water molecules of crystallization not shown for clarity); see Table 1 for details.  $[\text{Fe}(\text{DABP})_3]^{2+}$  units lying in front are shown with black bonds, those lying behind are depicted with grey bonds. Additional symmetry relations:  ${}^1 = x, y, z-1; {}^{1'} = x, y, z+1; {}^{3'} = -x+1, -y+1, -z-2$ .

found between  $[\text{Fe}(\text{DABP})_3]^{2+}$  and  $\text{L}^2$ . The dicarboxylate moiety links two centrosymmetrically related metal cations as shown in Fig. 4. The packing in **4** can also be described, as in **3**, in terms of separated layers of  $[\text{Fe}(\text{DABP})_3]^{2+}$  or  $\text{L}^2$  units parallel to the *ab* plane which alternate along the *c* direction (see Fig. 5).

In the biphenyl-2,2'-dicarboxylate adduct  $[\text{Fe}(\text{DABP})_3](\text{L}^3) \cdot 12.5\text{H}_2\text{O}$  (**5**) there is only one hydrogen bond remaining between  $[\text{Fe}(\text{DABP})_3]^{2+}$  and  $\text{L}^3$ . All other amino or carboxylate groups are engaged into hydrogen bonding to water molecules of crystallization whose number reaches a maximum in this series here. In addition some weak N-H $\cdots$ N and O-H $\cdots$ N bonding can be found. As before, the packing in **5** can be described in terms of separated, loosely packed layers of  $[\text{Fe}(\text{DABP})_3]^{2+}$  or  $\text{L}^3$  units parallel to the *ab* plane which alternate along the *c* direction (see Fig. 6). The water molecules of crystallization assemble in chain substructures to fill the voids.

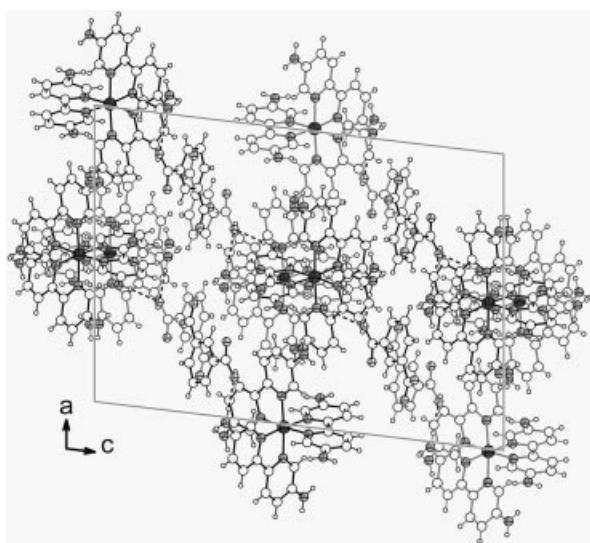
The layer arrangement in the structures of **3**, **4** and to some extent also **5** is highly similar to the packing in  $[\text{Fe}(\text{DABP})_3]\text{SO}_4 \cdot 9\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{DABP})_3]\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$  and  $[\text{Zn}(\text{DABP})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  which are constructed from alternating layers of the tris(chelate) cations and layers of the sulfate, chloride or nitrate anions together with water of crystallization [12].

A different hydrogen-bonding motif is observed with the trigonal ligand ( $\text{L}^4$ ) $^{3-}$  which is able to cap the triangular

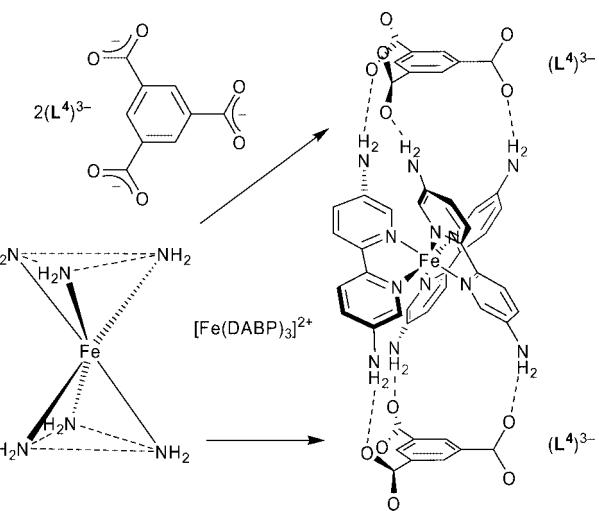


**Fig. 4** Centrosymmetrically related molecular entities of  $[\text{Fe}(\text{DABP})_3](\text{L}^2)$  in **4** showing the only two hydrogen bonds between  $[\text{Fe}(\text{DABP})_3]^{2+}$  and  $\text{L}^2$ ; see Table 1 for details. Additional symmetry relation:  ${}^5 = -x-2, -y-2, -z-1$ .

faces formed by three amino groups of  $[\text{Fe}(\text{DABP})_3]^{2+}$  so that supramolecular capsules are formed in the structure

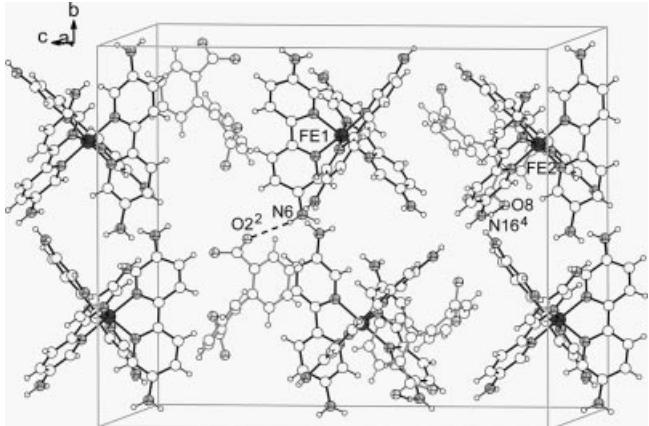


**Fig. 5** Packing diagram of  $[Fe(DABP)_3](L^2)$  in **4** with the hydrogen-bonding interactions (water molecules of crystallization not shown for clarity); see Table 1 for details.  $[Fe(DABP)_3]^{2+}$  and  $L^2$  units lying in front are shown with black bonds, those lying behind are depicted with grey bonds.



**Scheme 3** Schematic presentation of the triangular face-capping in  $[Fe(DABP)_3](L^4)_2 \cdot 20H_2O$  (**6**) by second-sphere hydrogen-bonding coordination.

configuration ( $\Delta$  in Fig. 8) opposite to the central Fe1 ( $\Lambda$  in Fig. 8).

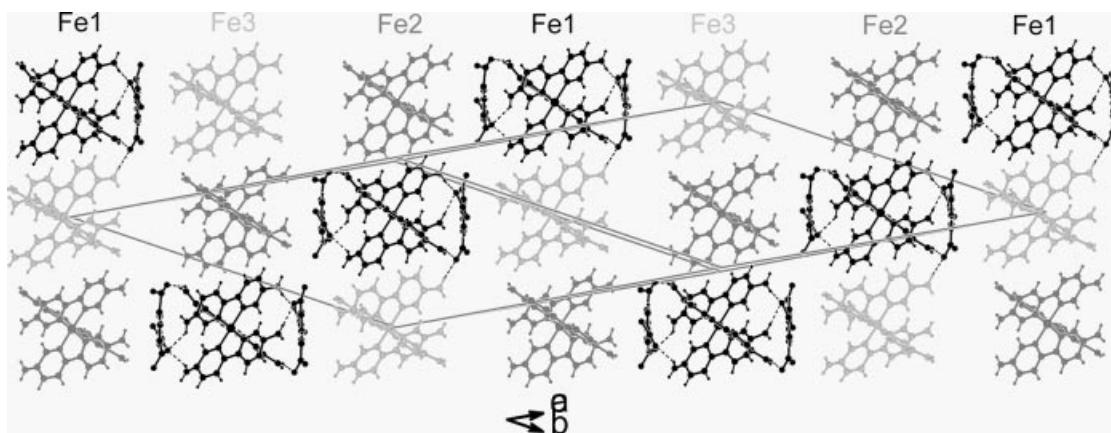


**Fig. 6** Packing diagram of  $[Fe(DABP)_3](L^3)$  in **5** showing the one single hydrogen-bonding interactions for each of the two independent molecules in the unit cell (water molecules of crystallization not shown for clarity); see Table 1 for details. For clarity the dicarboxylate moiety is drawn with grey bonds.

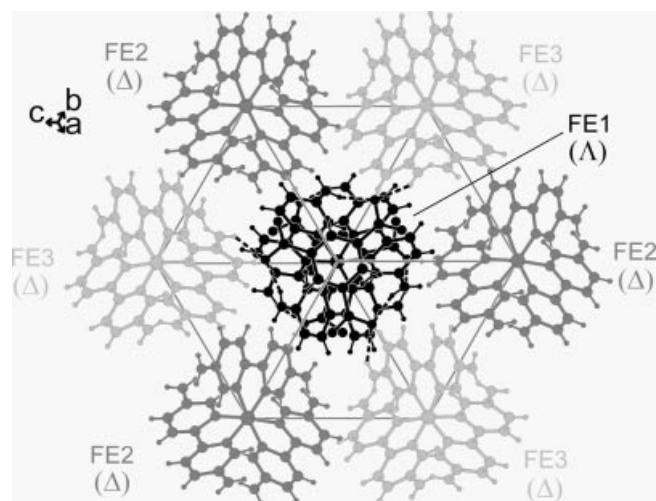
of compound **6**,  $[Fe(DABP)_3](L^4)_2 \cdot 20H_2O$  (Scheme 3). The threefold symmetry of the building blocks is preserved in the rhombohedral crystal system. The structure of **6** is constructed from three crystallographically different  $[Fe(DABP)_3]^{2+}$  moieties whose relative arrangement can be seen in Fig. 7 and 8. Noteworthy, in a sequence of  $\{Fe_2 \cdots L^4 - Fe_1 - L^4 \cdots Fe_3\}$  along the 111-direction (see Fig. 7) the three  $[Fe(DABP)_3]^{2+}$  moieties have the same  $\Lambda$  or  $\Delta$  configuration. Adjacent sequences along 111 are of opposite configuration. The Fe2 and Fe3 units surrounding a central  $\{L^4 - Fe_1 - L^4\}$  unit in the 111-plane all have the same

## Conclusions

The potential of the 5,5'-diamino-2,2'-bipyridine ligand, alone and in the tris(5,5'-diamino-2,2'-bipyridine)iron complex  $[Fe(DABP)_3]^{2+}$ , to enter into hydrogen bonding with suitable acceptor ligands has been demonstrated. A competition in hydrogen bonding with water molecules of crystallization also became evident. An increasing number of water molecules replaced the amino groups or vice-versa the carboxylate acceptor ligands in the hydrogen bonding interactions. Thus, in the series of compounds  $[Fe(DABP)_3](L^1) \cdot 5H_2O$ ,  $[Fe(DABP)_3](L^2) \cdot 8H_2O$  and  $[Fe(DABP)_3](L^3) \cdot 12.5H_2O$  the interaction between  $[Fe(DABP)_3]^{2+}$  and the dicarboxylate anions ( $L^1$ - $L^3$ ) decreases from a three-dimensional supramolecular network (with  $L^1$ ) to molecular units (with  $L^2$  and  $L^3$ ) with the increasing number of crystal water molecules. Hence, the weak cation-anion assembly in  $[Fe(DABP)_3](L^{1-3}) \cdot nH_2O$  is not too different from the packing in  $[M(DABP)_3]X \cdot nH_2O$  with the inorganic anions  $X = SO_4$ ,  $Cl_2$  and  $(NO_3)_2$  and  $M = Fe$ ,  $Ni$  and  $Zn$ , respectively [12]. To enable a more straightforward design of the second-sphere coordination with  $[Fe(DABP)_3]^{2+}$  it appears necessary to limit the number of crystal water molecules, for example by working in non-aqueous solvents. Also, a higher number of hydrogen-acceptor positions and a topological matching of donor and acceptor as with  $L^4$  in compound **6** seem to enhance the desired interactions. In addition, an increase of the negative charge density at the hydrogen-bond acceptor should also be advantageous in the competition with water molecules. Thus, the higher charge density at the oxo acceptor of the nitrophenolate anion led to the successful cavity design through molecular panelling in  $Fe^3(DABP)_3^{2+} [Fe^{2-}]$



**Fig. 7** Packing diagram in the 101-plane of  $[Fe(DABP)_3]_3(L^4)_2$  in **6** showing the face-capping of  $L^4$  towards the Fe1-moity and the arrangement of the three independent  $[Fe(DABP)_3]^{2+}$  units (in black – Fe1 with capping  $L^4$ , medium grey – Fe2 and light grey – Fe3; water molecules of crystallization not shown for clarity); see Table 1 for hydrogen-bonding details.



**Fig. 8** Packing diagram in the 111-plane of  $[Fe(DABP)_3]_3(L^4)_2$  in **6** showing the arrangement of the three independent  $[Fe(DABP)_3]^{2+}$  units (in black – Fe1 with capping  $L^4$ , medium grey – Fe2 and light grey – Fe3).

(DABP)<sub>3</sub>· $Fe^1(DABP)_3(nitrophenolate)_6^{2-}$  (see Scheme 2) despite the presence and crystallization from water [18]. Whereas in a carboxylate group the negative charge is delocalized over two oxygen atoms leading to a smaller negative charge density at each possible H-bond accepting oxygen atom. Further work involving the supramolecular chemistry of  $[Fe(DABP)_3]^{2+}$  is in progress, thereby aiming at a utilization of the threefold symmetry and potential  $\Lambda/\Delta$ -chirality in combination with chiral hydrogen-acceptor ligands.

## Experimental Part

NMR spectra were recorded on a Bruker Avance DPX 200 spectrometer (200.1 MHz) with calibration against the solvent signal ( $DMSO-d_6$  2.50 ppm and  $D_2O$  4.70 ppm). Elemental analyses were done on a VarioEL from Elementaranalysensysteme GmbH.

The ligand 5,5'-bis(ethoxycarbonylamino)-2,2'-bipyridine (BEBP, **1**) and the iron(II) complexes  $[Fe(DABP)_3]SO_4$  and tris[tris(5,5'-diamino-2,2'-bipyridine)iron(II)] bis(benzene-1,3,5-tricarboxylate) 20hydrate,  $[Fe(DABP)_3]_3(L^4)_2 \cdot 20H_2O$  (**6**) were prepared following previously published procedures [12,13,]. Colorless isometric crystals for the structural investigation of **1** were obtained from ethanol. Compound **6** was crystallized from hot  $H_2O$ . The second-sphere ligands, namely the disodium salt of terephthalic acid (sodium terephthalate,  $Na_2L^1$ , Aldrich), isophthalic acid ( $H_2L^2$ , Acros), biphenyl-2,2'-dicarboxylic acid ( $H_2L^3$ , Acros), and benzene-1,3,5-tricarboxylic acid (trimesic acid) ( $H_3L^4$ , Aldrich) were commercial products and used as received.

## Synthesis

**5,5'-Diamino-2,2'-bipyridine, DABP (2).** The ligand was prepared using a modification of the procedure described in ref. 12, 27: In a 250 ml three-necked flask were placed 2.37 g (10 mmol) of nickel dichloride hexahydrate and 10.5 g (40 mmol) of triphenyl phosphine. The flask was evacuated and refilled with argon for three times. 100 ml of dried dimethyl formamide (DMF) was added under inert gas and the solution rapidly turned blue. After  $PPh_3$  and  $NiCl_2 \cdot 6 H_2O$  had completely dissolved in DMF, 0.7 g (11 mmol) of zinc powder was added to the solution under inert gas at 50 °C and the solution slowly turned brown-red. After stirring this mixture for 1 h, 10 ml of a DMF solution with 1.28 g (10 mmol) of 5-amino-2-chloro-pyridine was added dropwise into the mixture. Stirring was continued for 4 h at 50 °C at which time the starting material could not be detected anymore by thin-layer chromatography (eluent ethyl acetate). The reaction mixture was then narrowed in vacuum to half of its volume. After adding 250 ml of water the mixture was carefully poured into 150 ml of conc. ammonia. The ammonia had to be really concentrated. After addition of aqueous  $NH_3$  the mixture was warmed to 40–50 °C (maximum of 50 °C, because at higher temperature the Ni-DABP complex would form). Some gaseous  $NH_3$  was bubbled through the mixture to ensure a high  $NH_3$  concentration. The warm solution was stirred for 1–2 days. To compensate for the loss of  $NH_3$  during this time from the warm solution, gaseous  $NH_3$  was bubbled through the mixture from time to time. The solution turned blue because of the formation of hexaammin-nickel(II) complexes. The  $PPh_3$  precipitate was removed by fil-

tration and the filtrate was extracted three times with 50 ml of dichloromethane each. The combined organic phases were treated with 50 ml of half-concentrated HCl for three times each to separate the diamino-bipyridine from  $\text{PPh}_3$ . During this procedure strongly colored diamino-dihydro-dichlorides formed. The combined acidic aqueous phases were carefully neutralized with a 10 %  $\text{Na}_2\text{CO}_3$  solution. The product **2** separated as a yellowish solid and was sublimed (0.001 bar, temperature 20 °C below melting point of 205 °C) to give a colorless powder (yield >1 g, >55 %). One further critical point is also the workup procedure upon extraction of the aqueous filtrate after  $\text{PPh}_3$  removal by filtration: 5,5'-diamino-2,2'-bipyridine is fairly bad soluble in the common solvents used for extraction (ethyl acetate, dichloromethane). This means that one sometimes could see some insoluble material between the aqueous phase (ammonia and its nickel-complexes) and the yellowish organic phase. If this is the case, the above treatment of the *filtered* organic phase with acid (to remove  $\text{PPh}_3$ ) leads to a substantial loss of product. To avoid this, filtration, drying and subsequent sublimation of the collected insoluble solids is an elegant way for a high yield isolation of the product. – Repeated preparations of **2** by the above route showed that the purity of the solvents does not affect the reaction. Also commercially available  $\text{PPh}_3$  and the nickel-salts are generally pure enough for this route. Analytical data corresponded to published values of **2** [12, 27]. Colorless isometric crystals for the structural investigation of **2** were obtained from ethanol/water.

**[Tris(5,5'-diamino-2,2'-bipyridine)iron(II)] benzene-1,4-dicarboxylate pentahydrate,  $[\text{Fe}(\text{DABP})_3](\text{L}^1)\cdot 5\text{H}_2\text{O}$  (**3**)**.  $[\text{Fe}(\text{DABP})_3]\text{SO}_4$  (36 mg, 0.05 mmol) and disodium terephthalate ( $\text{Na}_2\text{L}^1$ ) (11 mg, 0.05 mmol) were heated in 10 mL of  $\text{H}_2\text{O}$  to 90 °C. The resulting red solution was cooled to room temperature and the solvent was allowed to slowly evaporate. After a week, dark-red prismatic crystals formed (crystal yield: 23 mg, 59 %). Calc. for  $\text{C}_{38}\text{H}_{34}\text{N}_{12}\text{O}_4\text{Fe}\cdot 5\text{H}_2\text{O}$  (868.70): C 52.54, H 5.11, N 19.35. Found C 51.96, H 5.51, N 18.82 %.

**$^1\text{H NMR}$  ( $\text{DMSO}-d_6$ ):** δ 8.00 (d, 6H, H<sub>3,3'</sub>,  $J$  = 8.8 Hz), 7.81 (s, 4H, phenyl), 7.07 (dd, 6H, H<sub>4,4'</sub>,  $J_1$  = 8.8 Hz,  $J_2$  = 2.2 Hz), 6.58 (d, 6H, H<sub>6,6'</sub>,  $J$  = 2.2 Hz), 5.89 (s, 12H, -NH<sub>2</sub>).

**[Tris(5,5'-diamino-2,2'-bipyridine)iron(II)] benzene-1,3-dicarboxylate octahydrate,  $[\text{Fe}(\text{DABP})_3](\text{L}^2)\cdot 8\text{H}_2\text{O}$  (**4**)**.  $[\text{Fe}(\text{DABP})_3]\text{SO}_4$  (36 mg, 0.05 mmol) was reacted with  $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$  (16 mg, 0.05 mmol) by stirring the two materials in 5 mL of water for 0.5 h. The precipitated  $\text{BaSO}_4$  was removed by filtration. To the filtrate of the *in situ* prepared  $[\text{Fe}(\text{DABP})_3](\text{OH})_2$  was added isophthalic acid ( $\text{H}_2\text{L}^2$ ) (8 mg, 0.05 mmol). Dark-red prismatic crystals were obtained after 2 weeks (crystal yield 25 mg, 64 %). Calc. for  $\text{C}_{38}\text{H}_{34}\text{N}_{12}\text{O}_4\text{Fe}\cdot 8\text{H}_2\text{O}$  (922.73): C 49.46, H 5.46, N 18.22. Found C 49.36, H 5.48, N 18.71 %.

**$^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):** δ 8.26 (t, 1H, phenyl-2,  $J$  = 1.4 Hz), 7.98 (d, 6H, H<sub>3,3'</sub>,  $J$  = 8.8 Hz), 7.92 (dd, 2H,  $J_1$  = 7.6, phenyl-4,6,  $J_2$  = 1.4 Hz), 7.41 (t, 1H, phenyl-5,  $J$  = 7.6 Hz), 7.27 (dd, 6H, H<sub>4,4'</sub>,  $J_1$  = 8.8,  $J_2$  = 2.4 Hz), 6.80 (d, 6H, H<sub>6,6'</sub>,  $J$  = 2.4 Hz).

**[Tris(5,5'-diamino-2,2'-bipyridine)iron(II)] biphenyl-2,2'-dicarboxylate 12.5H<sub>2</sub>O,  $[\text{Fe}(\text{DABP})_3](\text{L}^3)\cdot 12.5\text{H}_2\text{O}$  (**5**)**. Compound **5** was prepared by a similar procedure to compound **4** except that biphenyl-2,2'-dicarboxylic acid ( $\text{H}_2\text{L}^3$ ) (12 mg, 0.05 mmol) was used instead of isophthalic acid ( $\text{H}_2\text{L}^2$ ). Dark-red prismatic crystals of complex **5** were obtained (crystal yield 38 mg, 80 %). Calc. for  $\text{C}_{44}\text{H}_{38}\text{N}_{12}\text{O}_4\text{Fe}\cdot 12.5\text{H}_2\text{O}$  (1079.90): C 48.94, H 5.88, N 15.56. Calc. for  $\text{C}_{44}\text{H}_{38}\text{N}_{12}\text{O}_4\text{Fe}\cdot 6\text{H}_2\text{O}$  (962.80): C 54.89, H 5.23, N 17.46. Found C 54.66, H 5.40, N 17.56 %.

**$^1\text{H NMR}$  ( $\text{DMSO}-d_6$ ):** δ 8.00 (d, 6H, H<sub>3,3'</sub>,  $J$  = 8.6 Hz), 7.37–7.31 (m, 6H, phenyl), 7.06 (d, 6H, H<sub>4,4'</sub>,  $J$  = 8.6 Hz), 6.91 (m, 2H, phenyl), 6.58 (s, 6H, H<sub>6,6'</sub>), 5.90 (s, 12H, -NH<sub>2</sub>).

## Structure determinations

**Data Collection:** Siemens Bruker Smart AXS with CCD area detector for compounds **1–3** and **5**, Rigaku R-AXIS RAPID IP diffractometer (with rotating anode) for compound **4**, Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), graphite monochromator,  $\omega$ -scan method for **1–3** and **5**, oscillation method for **4**; data collection and cell refinement with SMART [28], data reduction with SAINT [28], experimental absorption correction with SADABS [29]. The data were corrected by multi-scan absorption for complex **2**, **3** and **5**, and by empirical absorption correction ( $\gamma$ -scans) for **4**. **Structure Analysis and Refinement:** All structures were solved by direct methods (SHELXS-97) [30]; refinement was done by full-matrix least squares on  $F^2$  using the SHELXL-97 program suite [30]. All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on carbon were calculated using appropriate riding models (AFIX 43 for aromatic CH, AFIX 23 for  $\text{CH}_2$ , AFIX 33 for  $\text{CH}_3$ ) and isotropic temperature factor of  $U(\text{H})$  = 1.2 Ueq(C) for CH and  $\text{CH}_2$  and  $U(\text{H})$  = 1.5 Ueq(C) for  $\text{CH}_3$ . In **1**, **2** and **3** hydrogen atoms on nitrogen (NH<sub>2</sub>, NH) and oxygen (crystal water) were found and their positional parameters refined with isotropic temperature factors of  $U(\text{H})$  = 1.2 Ueq(N/O). In the final stages of the refinement of **3** the hydrogen atoms on O<sub>7</sub> and O<sub>9</sub> had to be kept fixed (AFIX 1/0). In **4** and **5** the hydrogen atoms on nitrogen (NH<sub>2</sub>) were calculated using AFIX 93 as a riding model and isotropic temperature factors of  $U(\text{H})$  = 1.2 Ueq(C). Hydrogen atoms on oxygen (crystal water) were initially found and then fixed during subsequent refinement (AFIX 1/0) with isotropic temperature factors of  $U(\text{H})$  = 1.2 Ueq(N/O). Hydrogen atoms for O<sub>9</sub> and O<sub>13</sub> in **4** and for O<sub>22</sub> in **5** were not found but included in the formula sum and weight. Refinement of the crystal structures for compound **4** and **5** was hampered by disorder in the crystal water substructure; the  $[\text{Fe}(\text{DABP})_3](\text{L})$  moiety could be clearly refined, however.

Graphics were obtained with DIAMOND [31]. Crystal data and details on the structure refinement are given in Table 3. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-240919 for **1**, CCDC-240920 for **2**, CCDC-240921 for **3**, CCDC-240922 for **4**, CCDC-240923 for **5**, CCDC-185557 for **6**).

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