

Self host–guest network through molecular paneling of *para*-nitrophenolate: hydrogen-bonded assembly of three tris(5,5'-diamino-2,2'-bipyridine)iron complexes in the crystallographic asymmetric unit

Xiao-Juan Yang, Biao Wu and Christoph Janiak*

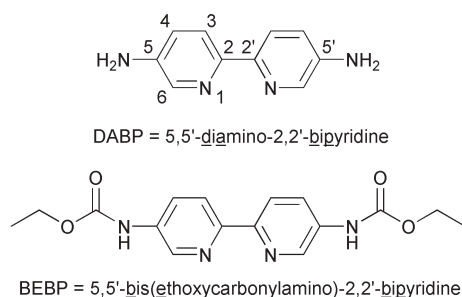
Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr 21, D-79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de; Fax: 49 761 2036147; Tel: 49 761 2036127

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The second-sphere hydrogen-bonding interaction of one out of three tris(diamino-bipyridine)iron complexes, $[\text{Fe}^1(\text{DABP})_3]^{2+}$, in the crystallographic asymmetric unit with nitrophenolate leads to a cavity created by the nitrophenolate panels whose space is filled through self-inclusion of a crystallographically different $[\text{Fe}^2(\text{DABP})_3]^{2+}$ -cation (DABP = 5,5'-diamino-2,2'-bipyridine).

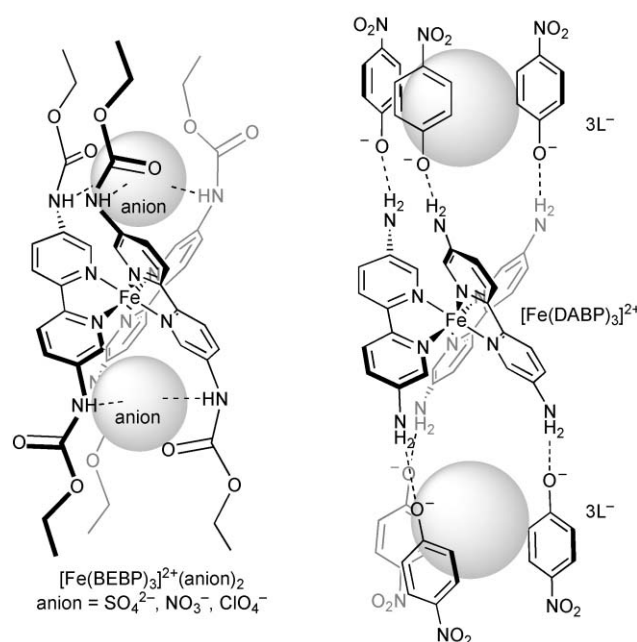
The field of crystal engineering is of growing interest and numerous work has been done on the assembly of supramolecular systems such as host–guest recognition, inclusion and encapsulation, *etc.*^{1,2} Many efforts in this field have focused on the predictable assembly of organic molecular solids and metal coordination compounds (coordination polymers).^{3–6} 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 A variety of biochemical systems utilize second-sphere coordination for the modification of the chemistry around metal ions.^{9,10} In order to enact 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)^{11,12} and derivatives such as BEBP^{13,14} possess the dual functions. Only the bipyridine nitrogen atoms but not the amino groups were found capable of coordinating to a metal ion, yielding the primary complex, *e.g.* $[\text{M}(\text{DABP})_3]^{2+}$. 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 DABP ligand have been found to enter into N–H...O hydrogen bonding to water molecules

of crystallization or in N–H...X hydrogen bonding to anions (X = SCN^- , SO_4^{2-} , Cl^-) or acceptor ligands in $\text{M}(\text{DABP})_3\text{X}_2$ moieties (X = Cl, N_3).¹¹ The second-sphere coordination of $[\text{M}(\text{DABP})_3]^{2+}$ complexes with crown ethers led to the supramolecular assemblies of $\{[\text{Ni}(\text{DABP})_3] \cdot (18\text{-C-6})\} \text{Cl}_2 \cdot 4\text{CH}_3\text{OH}$ (kinked 2₁-helical chain) and $\{[\text{Zn}(\text{DABP})_3] \cdot (18\text{-C-6})\} (\text{NO}_3)_2 \cdot 3/8\text{H}_2\text{O}$ (linear strands).¹² 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).^{13,15} 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. The orientation of the six amino groups in complexes $[\text{M}(\text{DABP})_3]^{2+}$ should allow for the extension of the two triangular clefts, for example, by attaching hydrogen-bond acceptor groups (*e.g.* nitrophenolate = L), as visualized in Scheme 1, right.

A supramolecular compound of formula $[\text{Fe}^3(\text{DABP})_3]^{2+} [\text{Fe}^2(\text{DABP})_3 \text{C}(\text{nitrophenolate})_6]^{2-}$ (**1**) could be obtained by co-crystallization of $[\text{Fe}(\text{DABP})_3]^{2+}$ with nitrophenolate as hydrogen-bond acceptor ligand.† Compound **1**



Scheme 1 Cleft formation based on metal complexes with 5,5'-disubstituted-2,2'-bipyridine ligands; L = nitrophenolate.

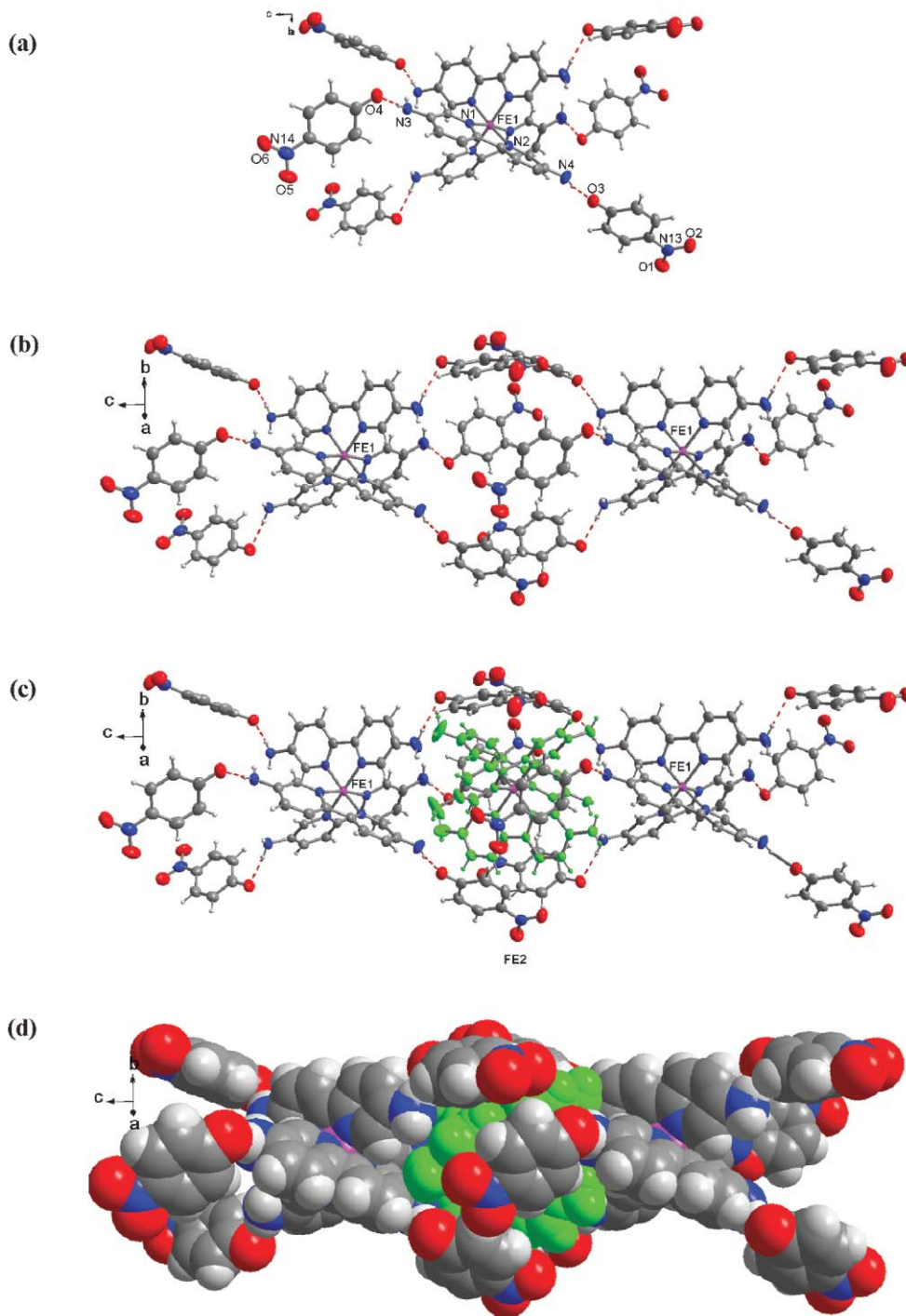


Fig. 1 (a) The structure of $\{[\text{Fe}^1(\text{DABP})_3](\text{nitrophenolate})_6\}^{4-}$ units showing the interactions between $-\text{NH}_2$ and nitrophenolate. Hydrogen bond distances: $\text{N}3 \cdots \text{O}4$ and $\text{N}4 \cdots \text{O}3$, see Table 1. Click here to access a 3D view of Fig. 1a. (b) Chain arrangement of the $\{[\text{Fe}^1(\text{DABP})_3](\text{nitrophenolate})_6\}^{4-}$ units along c with cavity formation through the nitrophenolate panels. Click here to access a 3D view of Fig. 1b. (c) Cavity filled with a crystallographically different $[\text{Fe}^2(\text{DABP})_3]^{2+}$ unit (in green). (d) Space-filling representation of (c). Click here to access a 3D view of Fig. 1c.

consists of three crystallographically different kinds of $[\text{Fe}(\text{DABP})_3]^{2+}$ moieties, with the iron centers termed Fe^1 , Fe^2 and Fe^3 for distinction.‡ The pseudo-octahedral tris(chelate)–metal environment in the first-sphere complexes $[\text{Fe}(\text{DABP})_3]^{2+}$ in **1** is typical and will not be detailed any further here but has been described in the parent compound $[\text{Fe}(\text{DABP})_3]\text{SO}_4$ and in other $[\text{Fe}(\text{bipy})_3]^{2+}$ complexes (bipy = 2,2'-bipyridine).^{11,12,16}

The first kind of $[\text{Fe}^1(\text{DABP})_3]^{2+}$ units form hydrogen bonds with six nitrophenolate acceptor ions (*cf.* Scheme 1). Each $-\text{NH}_2$ group binds one *p*-nitrophenolate through one of the hydrogen atoms in NH_2 to the deprotonated hydroxyl oxygen

atom of the nitrophenolate. As a result, two oppositely-located bowls or clefts are formed (Fig. 1a). Along c , these moieties are arranged in a chain with the nitrophenolate groups of neighboring moieties interdigitating. These six interdigitating *p*-nitrophenolate groups create a large, olive-shaped cavity between the $\{[\text{Fe}^1(\text{DABP})_3](\text{nitrophenolate})_6\}^{4-}$ moieties (Fig. 1b). These cavities contain a crystallographically different $[\text{Fe}^2(\text{DABP})_3]^{2+}$ unit (Fig. 1c).

There are only weak $\text{N}-\text{H} \cdots \text{N}$ bonds between the Fe^1 and Fe^2 units ($\text{N}3 \cdots \text{N}8$, $\text{N}7 \cdots \text{N}4$, $\text{N}8 \cdots \text{N}3$, see Table 1) and no hydrogen bonds from the Fe^2 molecule to the nitrophenolate panels within the chain. The chain depicted in Fig. 1c is still an

Table 1 Hydrogen bonding interactions in **1**^a

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]	Sym. rel.
Fe¹ chain					
N3–H3B···O4	0.91(3)	1.99(3)	2.892(3)	174(2)	5
N4–H4B···O3	0.86(3)	2.05(3)	2.888(3)	166(3)	5 ₅₅₄
intra–Fe ² CFe ¹ chain:					
N3–H3A···N8	0.88(3)	2.44(3)	3.307(3)	170(2)	4 ₅₄₅
N7–H7B···N4	0.85(4)	2.43(4)	3.277(4)	172(3)	4 ₆₅₅
N8–H8B···N3	0.91(3)	2.33(3)	3.220(3)	167(2)	5 ₅₅₄
inter–Fe ² CFe ¹ chain:					
N8–H8A···O3	0.85(3)	2.07(3)	2.911(3)	166(2)	5 ₅₅₄
Fe³ chain:					
N12–H12B···N11	0.89(3)	2.36(3)	3.204(3)	159(2)	4
interchain interactions through water molecules:					
N11–H11C···O02	0.97(3)	2.21(3)	3.117(3)	155(2)	4 ₅₅₄
N12–H12A···O01	0.86(3)	2.15(3)	3.007(3)	176(3)	4
O01–H01A···O4	0.97(3)	1.73(3)	2.700(3)	174(4)	
O01–H01B···O2	0.83(3)	2.31(3)	3.068(2)	153(3)	3 ₆₆₅
O02–H02A···O6	0.75(4)	2.34(4)	3.066(3)	164(4)	
O02–H02B···O3	0.88(4)	2.01(4)	2.877(3)	172(4)	

^a D = Donor, A = Acceptor. Principal symmetry relations (without translation): 3 = $-x + y, -x, z$; 4 = $y, x, z + 1/2$; 5 = $x - y, -y, z + 1/2$.

anionic substructure of formula $[\text{Fe}^2(\text{DABP})_3\text{CFe}^1(\text{DABP})_3(\text{nitrophenolate})_6]^{2-}$ in the overall crystal structure of **1**. The charge is compensated by a collinear chain of N–H···N

linked crystallographically independent $[\text{Fe}^3(\text{DABP})_3]^{2+}$ cations (Fig. 2; N12···N11, see Table 1). Water molecules (O01, O02) link the chains of Fe³ and Fe²CFe¹ through hydrogen bonding (see Table 1). Fig. 3 illustrates the packing of the two different collinear chains along *c*. Between the nitrophenolate anions and the pyridyl rings, C–H···π and some π–π interactions can be found.^{17,18} The latter are unremarkable, however, and mostly exhibit rather long centroid–centroid distances (>3.9 Å), large slip angles ($>30^\circ$) and vertical displacements (>2.0 Å) between the ring centroids.¹⁸

Figs. 1c and d show that the crystal structure of **1** may be considered as a self host–guest system.¹⁹ The differences between the $[\text{Fe}^1(\text{DABP})_3]^{2+}$ host with its nitrophenolate panels and the $[\text{Fe}^2(\text{DABP})_3]^{2+}$ guest are at the conformational level. The $[\text{Fe}(\text{DABP})_3]^{2+}$ units are chiral. Interdigitating complexes of $\{[\text{Fe}^1(\text{DABP})_3](\text{nitrophenolate})_6\}^{4-}$ have the same (A/A) configuration (*A* in Fig. 1). The enclosed $[\text{Fe}^2(\text{DABP})_3]^{2+}$ guests are of opposite configuration (*A* in Fig. 1). $[\text{Fe}^3(\text{DABP})_3]^{2+}$ units in their chains have alternating A/A -configuration. In their directly adjacent chains, the $[\text{Fe}^1(\text{DABP})_3]^{2+}$ and $[\text{Fe}^2(\text{DABP})_3]^{2+}$ units are of respective opposite configuration. Yet, it is interesting to note that the overall hydrogen bonding network gives rise to a polar *c*-axis, hence the non-centrosymmetric polar space group $P3_1c$. Hydrogen bonding interactions from $[\text{Fe}(\text{DABP})_3]^{2+}$ complexes to chiral acceptors could be the basis for enantiomerically pure 1D single-stranded helical molecular networks.²⁰

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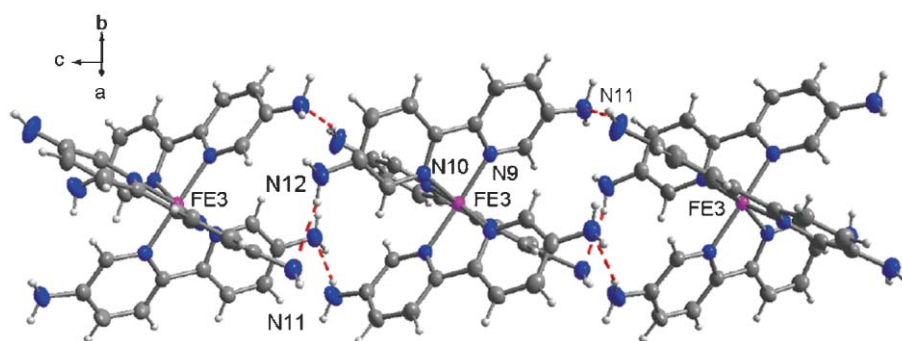


Fig. 2 Chain of the N–H···N linked $[\text{Fe}^3(\text{DABP})_3]^{2+}$ cations in **1**. Click here to access a 3D view of Fig. 2.

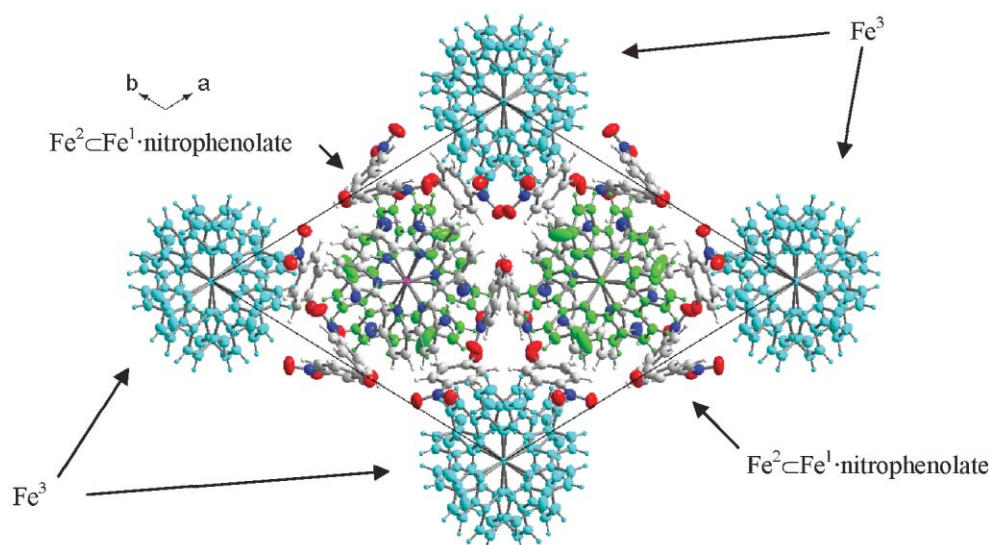


Fig. 3 Unit cell packing of the different chains of Fe³ (cyan colored) and Fe²CFe¹-nitrophenolate along *c* (Fe² unit colored in green). Interchain interactions through water of crystallization are not shown for clarity (see Table 1).

Notes and references

† Experimental: The ligand 5,5'-diamino-2,2'-bipyridine (DABP) and its iron(II) complex, $[\text{Fe}(\text{DABP})_3]\text{SO}_4$, were prepared following previously published procedures.^{11,21} Synthesis of [tris(5,5'-diamino-2,2'-bipyridine)iron(II)] bis(4-nitrophenolate) dihydrate (**1**): $[\text{Fe}(\text{DABP})_3]\text{SO}_4$ (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 BaSO_4 was removed by filtration. To the filtrate of the *in situ* prepared $[\text{Fe}(\text{DABP})_3](\text{OH})_2$ the 4-nitrophenol (14 mg, 0.10 mmol) was added. The mixture was stirred overnight at room temperature to form a red precipitate (22 mg, 50%). It was collected, washed with H_2O and recrystallized from H_2O to give dark-red prismatic crystals of compound **1**. ^1H NMR ($\text{DMSO}-d_6$, δ ppm): 8.00 (d, 6 H, H3,3', $J = 8.8$ Hz), 7.80 (d, 4 H, phenyl-3,5, $J = 9.4$ Hz), 7.07 (dd, 6 H, H4,4', $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz), 6.59 (d, 6 H, $J = 2.1$ Hz, H6,6'), 6.12 (d, 4 H, phenyl-2,6, $J = 9.4$ Hz), 5.91 (s, 12 H, $-\text{NH}_2$). $\text{C}_{42}\text{H}_{38}\text{N}_{14}\text{O}_6\text{Fe} \cdot \text{H}_2\text{O}$ (908.72): calc. C 55.51, H 4.44, N 21.58; $\text{C}_{42}\text{H}_{38}\text{N}_{14}\text{O}_6\text{Fe} \cdot 2\text{H}_2\text{O}$ (926.75): calc. C 54.43, H 4.57, N 21.16; found C 55.42, H 4.97, N 21.22%.

‡ X-ray crystallography: All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on carbon were calculated (AFIX 43 for aromatic CH, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$). Hydrogen atoms on nitrogen and oxygen (crystal water) were found and refined with isotropic temperature factors of $U(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ and $U(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. $\text{C}_{42}\text{H}_{42}\text{FeN}_{14}\text{O}_8$, $M = 926.75$, crystal size $0.30 \times 0.20 \times 0.15$ mm³, hexagonal, $P3_1c$, $a = 19.3682(7)$, $c = 18.9884(10)$ Å, $V = 6168.8(5)$ Å³, $Z = 6$, $T = 153(2)$ K, θ range 1.21–27.97°, $\mu(\text{Mo K}\alpha) = 0.441$ mm⁻¹, $F(000) = 2892$, $D_{\text{calc}} = 1.497$ g cm⁻³, 36314 reflections collected, 9443 unique ($R_{\text{int}} = 0.0306$), 8633 observed [$I > 2\sigma(I)$], 634 parameters, final $R1/wR2$ [$I > 2\sigma(I)$] = 0.0383/0.0806, final $R1/wR2$ (all data) = 0.0427/0.0826, goodness-of-fit on $F^2 = 1.047$, Flack parameter²² = -0.002(12). Graphics were obtained with DIAMOND.²³ Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as spheres of arbitrary radii. CCDC reference number 234097. See <http://www.rsc.org/suppdata/ce/b4/b404151h/> for crystallographic data in CIF format.

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