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2,6-Di(pyrazol-3-yl)pyridine as meridional capping ligand: Synthesis, characterization and crystal structure of the first corresponding hexanuclear iron(III) complex

Daniel Plaul,^[a] Eike T. Spielberg,^[a] and Winfried Plass*^[a]

Dedicated to Professor Gerd Becker on the occasion of his 70th birthday

Abstract. Based on the 2,6-di(pyrazol-3-yl)pyridine ligand (H_2 bpp) the hexanuclear iron(III) complex $[Fe_6(bpp)_4(\mu_3-O)_2(\mu-OMe)_3(\mu-OH)Cl_2]$ (**1**) has been synthesized. The reaction with iron(II) chloride and additional pyridine leads to the exclusive formation of the complex through self-assembly process. Six octahedrally coordinated iron centers are linked through the pyrazolido groups of four H_2 bpp ligands. These are further linked through bridging hydroxido, methoxido, and oxido groups. The complex has been characterized by IR spectroscopy, ESI mass spectrometry, elemental analysis and X-ray crystallography. Temperature-dependent magnetic measurements indicate strong antiferromagnetic exchange interaction between the high-spin iron(III) centers within the complex leading to an $S = 0$ spin ground state. As a result of the two $Fe_3(\mu_3-O)$ fragments two frustrated exchange pathways are present. In addition the properties of H_2 bpp as a potential capping ligand for the synthesis of heteroleptic trinuclear complexes based on the triaminoguanidine core is investigated.

Keywords: Iron; Hexanuclear complex; Magnetic properties; Pyrazole-based ligand; X-ray diffraction.

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Introduction

The 2,2':6',2''-Terpyridine (terpy) and its derivatives are widely used ligands in coordination chemistry [1,2]. Terpy can bind to both low- and high-oxidation state metal ions, almost always in a tridentate fashion [1,3]. While terpy ligands have been intensely studied due to their commercial accessibility as well as straightforward synthetic access, the analogues pyrazolyl ligands have been less investigated [4]. Especially the 2,6-di(pyrazol-3-yl)pyridine ligand (H_2 bpp) shown in Scheme 1 has only scarcely been utilized.

This ligand is known to form mononuclear homoleptic iron(II) complexes of the general formula $[Fe(H_2 \text{ bpp})_2]X_2$ which are stable in air and undergo temperature induced spin crossover [5–10]. While the temperature of these transitions vary considerably, it can be generalized that hydration of the compounds tends to favor the low-spin state of the iron center. Besides only a few cobalt(II), nickel(II) and copper(II) complexes as well as the corresponding lanthanide complexes with three ligand molecules of the general formula $[Ln(H_2 \text{ bpp})_3][PF_6]_3$ have been described in literature [9,11–13]. All these complexes are found to be exclusively mononuclear, independent of the central metal ion. Although the ligand system offers with the second nitrogen atom of the pyrazolyl moieties two additional potential donor groups, no covalently linked dinuclear or oligonuclear complexes of divalent metal ions have been reported until now. Nevertheless, deprotonation of the pyrazole NH groups should provide an access to higher nuclearity aggregates. This has been proven for derivatives with the methyl and phenyl substituents at the 5-position of the pyrazole rings of the ligand system leading to octanuclear copper(I) complexes [14]. The H_2 bpp ligand system can be considered as ideal candidate for meridional capping of octahedral complex fragments, which in addition might be able to introduce spin-crossover properties. A prototypical case for which capping has been utilized with similar tridentate ligands is the trinuclear core fragment based on the tritopic triaminoguanidine ligand [15].

Herein we report on attempts to synthesize appropriate heteroleptic trinuclear complexes with H_2 bpp as capping ligand. This finally resulted in the synthesis of the first hexanuclear iron(III) complex $[Fe_6(\text{bpp})_4(\mu_3\text{-O})_2(\mu\text{-OMe})_3(\mu\text{-OH})Cl_2]$ (1) with the parent bispyrazolyl-pyridine ligand system.

Results and Discussion

Synthesis and Characterization

The ligand H_2 bpp was obtained in a two step synthesis through condensation of 2,6-diacetylpyridine with *N,N*-dimethylformamide diethyl acetal and subsequent formation of the heterocycles with hydrazine in nearly quantitative yield [16]. With this tridentate capping ligand we attempted the synthesis of heteroleptic trinuclear iron complexes based on the tritopic triaminoguanidine core fragment represented in Scheme 2. We have previously employed this tritopic core fragment in the synthesis of trinuclear octahedral nickel(II) complexes [17] and as building block for the generation of copper(II) coordination polymers [18,19].

Iron(II) chloride has generally been used as starting material in all experiments, which is added to a solution of the triaminoguanidine core ligand containing the appropriate base to account for its deprotonation. The solution immediately turns reddish or greenish indicating initial coordination of the iron center, although the actual color depends on the solvent (DMF or pyridine) and whether aerobic or anaerobic conditions are employed.

If the reaction is run under anaerobic conditions in DMF as solvent and triethylamine as base, after addition of the H_2 bpp ligand the homoleptic complex cation $[Fe(H_2\text{bpp})_2]^{2+}$ is obtained from the initially red solution, which has been identified by comparison of the spectroscopic data with an authentic sample [5]. A similar phenomenon is observed when the reaction is run in pyridine as solvent, which also acts as the needed base. Under these conditions from the red solution $[Fe(py)_4Cl_2]$ [20,21] is obtained as the sole iron species. Both cases are indicative for a stabilization of the homoleptic and mononuclear species with respect to the heteroleptic trinuclear arrangement and consequently results in the extraction of the metal ion from the pre-built trinuclear core.

Under aerobic conditions in DMF with triethylamine as base the initial reaction solution immediately turns deep green and within minutes the precipitation of dark colored unidentified products is observed. This cannot be prevented by the addition of the potential capping ligand H_2 bpp, even if this co-ligand is added without any delay in the reaction sequence. On the other hand, when pyridine is used as solvent the initially red reaction solution intensifies its color upon the addition of the H_2 bpp ligand. From the final reaction solution a red crystalline material could be isolated in high yield, which does not contain the triaminoguanidine ligand. This again leads to the extraction of the metal ion from the core ligand fragment. The isolated compound could be characterized as the hexanuclear iron(III) complex $[Fe_6(bpp)_4(\mu_3-O)_2(\mu-OMe)_3(\mu-OH)Cl_2]$ (**1**) with a deprotonated bispyrazolyl-pyridine ligand system.

The hexanuclear iron(III) complex **1** can also be deliberately synthesized in absence of the triaminoguanidine ligand. In this case iron(II) chloride is dissolved in a pyridine/methanol (1:1) mixture and the H_2 bpp ligand is added to this solution. This sequence is chosen in order to prevent the formation of the homoleptic mononuclear iron(II) complex. The pyridine acts both as solvent and base. During complexation the iron(II) ions are oxidized. The deprotonation of the two acidic pyrazole protons allows further aggregation and leads to the formation of the hexanuclear complex $[Fe_6(bpp)_4(\mu_3-O)_2(\mu-OMe)_3(\mu-OH)Cl_2]$ (**1**) through self-assembly process. Complex **1** has been characterized by IR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography.

The IR spectra of complex **1** show several characteristic features supporting the given composition and structure. At first the NH stretching vibration in the free ligand observed at about 3200 cm^{-1} is absent in the spectra of the isolated compound, which is consistent with the full deprotonation of the pyrazolyl groups in the ligand. This clearly indicated the absence of the homoleptic mononuclear iron(II) complex cation $[Fe(H_2\text{bpp})_2]^{2+}$ as potential byproduct in this reaction. Characteristic bands are observed at 2918 and 2814 cm^{-1} , which can be assigned to the asymmetric and symmetric stretching vibration of the methyl groups of the bridging methoxido ligands. The band of the OH stretching vibration of the bridging hydroxido group is observed at 3435 cm^{-1} . In addition also a very strong and broad band is observed at 493 cm^{-1} due to the iron-chloride stretching vibration.

In the positive ion electrospray (ESI) mass spectrum the base peak is observed at an m/z value of 1349 which can be assigned to the hexanuclear iron complex which lost one of the coordinated chloride ions. Moreover, an additional intense signal is observed at $m/z = 1313$ due to the loss of the second coordinated chloride ion accompanied by a proton.

Description of the structure

The hexanuclear iron(III) complex **1** crystallizes in the monoclinic space group $P2_1$. The molecular structure as well as the heteroatom labeling scheme of the complex molecule is

depicted in Figure 1. The structure of the central Fe_6 core unit is enlarged in Figure 2. Selected bond lengths and angles are listed in Table 1.

Four iron centers (Fe1, Fe2, Fe3, and Fe4) are coordinated by the deprotonated meridional capping ligand bpp^{2-} in its terpy-like coordination pocket. The pyrazolido fragments are coordinated to two additional iron centers (Fe5 and Fe6) leading to a paddle-wheel structure with an additional chloride ion coordinated at both iron centers forming the corresponding axle. The four planar $\{\text{Fe(III)bpp}\}^+$ subunits in the paddle wheel are arranged perpendicular to each other and further linked by one μ -OH and three μ -OMe bridging groups. In addition both iron centers (Fe5 and Fe6) at the axle are further linked to two different $\{\text{Fe(III)bpp}\}^+$ subunits of the paddle wheel forming two $\text{Fe}_3(\mu_3\text{-O})$ fragments. The sixth coordination site of both iron(III) ions Fe5 and Fe6 are occupied by a chloride ion resulting in a neutral hexanuclear complex.

For all iron(III) ions a distorted octahedral coordination environment is observed with a N_3O_3 donor set for the iron centers Fe1, Fe2, Fe3, and Fe4, whereas a N_4OCl donor set is found for Fe5 and Fe6. For the latter two iron centers Fe5 and Fe6 this distortion is rather small, whereas for the four iron centers of the $\{\text{Fe(bpp)}\}^+$ subunits a severe distortion is observed as indicated by the relevant *trans* bridging angles (see Table 1). The small N–Fe–N *trans* angles of about 144° within the subunits are determined by rigid meridional capping ligand and the size of the large high-spin iron(III) ion. The formation of the Fe_3O fragments is related to the second set of small *trans* angles, as indicated by the O–Fe–N bond angles of about 154° between the pyridine donor of the bpp^{2-} ligand and the μ_3 -bridging oxygen atoms (O1 and O2).

These distortions lead to dissimilar Fe–N bond lengths of the two pyrazolido moieties of the ligand, depending on whether (206 pm) or not (218 pm) they are involved in the bridging of the Fe_3O fragments. This might be attributed to considerable differences regarding the structural *trans* effect of the relevant donors. The Fe–N bond lengths of the four pyridine nitrogen donors are with about 220 pm well within the expected range and somewhat longer than corresponding distances found for the pyrazolido nitrogen donors. The Fe–O bond lengths within the Fe_3O fragments are found at about 201 pm for the iron centers of the $\{\text{Fe(bpp)}\}^+$ subunits, whereas considerably shorter distances are found for Fe5 and Fe6 with about 193 pm. The two remaining coordination sites at the iron centers Fe1, Fe2, Fe3, and Fe4 are occupied by bridging oxygen atoms of methoxido and hydroxido groups with Fe–O distances of about 198 pm and 194 pm, respectively. Besides the μ_3 -bridging oxygen atoms (O1 and O2) the iron centers Fe5 and Fe6 are additionally coordinated by four nitrogen atoms of the pyrazolido moieties at distances ranging between 210 pm and 213 pm. The octahedral coordination environment of both iron centers is completed by a chloride ion coordinated at a distances of about 241 pm. The bond lengths for all iron centers are in the usually observed range typical for iron(III) high-spin complexes [22].

The iron centers within the complex are linked through three different types of bridges. Besides the linkages with μ -OMe, μ -OH, and μ_3 -O groups the iron centers are further linked through N–N diazine bridges of the pyrazolido moieties of the bpp^{2-} ligand (see Figure 2). The torsion angles of the diazine bridges are very similar and in the range between 170 and 180° due to the planarity of the $\{\text{Fe(bpp)}\}^+$ subunits (see Table 2). The bond angles at the bridging oxygen atoms are summarized in Table 3. The μ -O bridges can be divided into two groups according their bridging angle which is either close to 97° (O2M and O3M) or 111° (O1M and O1H). A similar observation is found for the μ_3 -O bridges with values of about 95° (O1 and O2) and 124° (O1M, O2M, O3M, and O1H). The smaller angles are

observed for the μ -OMe and μ_3 -O bridges connecting a pair of iron centers within the Fe_3O fragments ($\text{Fe1}\cdots\text{Fe2}$ and $\text{Fe3}\cdots\text{Fe4}$) leading to Fe_2O_2 units with rather short interatomic $\text{Fe}\cdots\text{Fe}$ distances of about 296 pm. All other $\text{Fe}\cdots\text{Fe}$ distances are clearly longer and in the range between 325 and 618 pm (see Table 4).

The obtained crystal structure is consistent with an overall neutral hexanuclear complex, as no indication for counterions can be found. Nevertheless, the actual protonation of the bridging oxygen atoms cannot be directly determined by X-ray crystallography. We therefore performed bond-valence sum (BVS) calculations to confirm the valence state of the iron ions in the complex and the protonation state of the bridging oxygen atoms. For iron compounds it has been shown, that BVS calculations with oxidation-state-independent parameters taken from the original reference of Brown and Altermatt [23], allow to distinguish between complexes of high-spin iron(II) ($\text{BVS} = 2.30 \pm 0.14$), high-spin iron(III) ($\text{BVS} = 3.04 \pm 0.12$), and the low-spin state of both iron(II) and iron(III) ($\text{BVS}(\text{Fe}^{2+}) = 4.22 \pm 0.23$ and $\text{BVS}(\text{Fe}^{3+}) = 4.10 \pm 0.34$) [24].

The relevant data for compound **1** is given in Table 5. The BVS values for the six iron centers are in good agreement with the oxidation and spin state of high-spin iron(III) ions. As the hydrogen atoms in the crystal structure of **1** could not be located and refined, the primarily obtained BVS values correspond to a non-protonated situation at the oxygen atoms. In the case of the twofold bridging oxygen atoms the primarily obtained BVS values clearly indicate that in the case of oxygen atom O1H an additional protonation is present, whereas the oxygen atoms OiM ($i=1,2,3$) are not protonated. This is consistent with three μ -OMe bridges (O1M, O2M, and O3M) and one μ -OH bridge (O1H). Moreover, the protonation of the μ -OH group is consistent with an observed hydrogen-bonding interaction towards the nitrogen atom N1PA of a co-crystallized pyridine molecule at a distance of 275 pm ($\text{O1H}\cdots\text{N1PA}$).

The situation is different for the μ_3 -O bridges, for which the calculated BVSs of about 1.6 are somewhat smaller than the expected value for an oxido group. It is therefore tempting to assume that an additional proton could be located at these oxygen atoms. If a single proton in a symmetric $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen-bridging mode ($\text{O1}\cdots\text{O2}$ 267 pm) is presumed to be present, the a BVS value of about two is obtained for the oxygen atoms O1 and O2. Although such $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen-bridges are well known for even shorter distances [25] and in the coordination environment of iron(III) ions [26,27], to the best of our knowledge, no such case has been reported for μ_3 -O groups in the vicinity of iron(III) ions. Nevertheless, in a seminal paper Day and Klemperer et al. [28] have reported for decavanadate that it is possible to protonate a triply-bridging oxygen, which in this case is even the preferred protonation site.

However, in the case of complex **1** such a protonation would necessitate a charge compensation, but neither an additional anion can be located in the crystal structure nor does the BVS analysis indicate the presence of an iron(II) ion. Moreover, the steric restraints at the μ_3 -oxido groups are unfavorable for such an $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonding. Also the rather basic reaction conditions with pyridine as solvent should not lead to such a protonation of the hexanuclear core. We therefore assign the unprotonated form at the μ_3 -oxido groups to the structure of complex **1** which is depicted in Figures 1 and 2. This interpretation is also consistent with the additional analytical data.

Magnetochemistry

The magnetic susceptibility data for the iron complex **1** has been measured in the temperature range from 2 to 300 K. The magnetic data are shown in Figure 3 as temperature-dependent plots of χ_M and $\chi_M T$. The $\chi_M T$ value at 300 K is $7.4 \text{ cm}^3 \text{ K mol}^{-1}$, which is significantly lower than the expected spin-only value for six independent high-spin iron(III) ions with

$S = 5/2$ ($26.26 \text{ cm}^3 \text{ K mol}^{-1}$ assuming that $g = 2$). On the other hand, this value is considerably higher than the spin-only value expected for six uncoupled low-spin iron(III) ions with $S = 1/2$ ($2.25 \text{ cm}^3 \text{ K mol}^{-1}$ assuming that $g = 2$) [29]. Upon lowering the temperature the $\chi_{\text{M}}T$ value steadily decreases almost linear, reaching values close to zero at temperatures below 5 K. Together with the very low room temperature value of $\chi_{\text{M}}T$, this temperature characteristic is indicative of an overall strong antiferromagnetic exchange interaction within the hexanuclear high-spin iron(III) core resulting in an $S = 0$ spin ground state.

Due to the topology of the hexanuclear core of compound **1** at least a three- J model is needed to describe the magnetic data. This is getting even more complicated when the actual variation of bridging groups and modes are considered. Beside the coupling through oxygen-based bridges (μ -OH, μ -OMe, and μ_3 -O), which is known to be very efficient, the interaction through the N–N diazine bridges of the ligand molecules has to be considered. Unfortunately, there is no analytical expression for the analysis of the magnetic interactions of a hexanuclear high-spin iron(III) complex with the given topology. On the other hand, the usual approach by diagonalizing the full spin-Hamiltonian matrix is hampered by large dimensions of the resulting matrix as well as the problem of overparametrization, as the large number of different exchange pathways within the hexanuclear core is considered. Moreover, the almost linear decrease of the $\chi_{\text{M}}T$ value with decreasing temperature clearly limits any attempt, not to say would makes it virtually impossible, to determine meaningful parameters from the magnetic data. We therefore did not attempt to extract any coupling parameters directly from the magnetic data.

On the other hand, magneto-structural correlations are known for iron(III) complexes, which allow to estimate relevant coupling constants. Most of these correlations are based on iron(III) systems containing dinuclear oxido-, hydroxido- and alkoxido-bridges. In all cases, correlations have been established between the exchange coupling constant J and the Fe–O–Fe angle (α) or the Fe–O distance (r) within the bridging units [30–34]. *Weihe* and *Güdel* used a formulation based on the angular overlap model to derive an expression for J including both parameters r as well as α represented in Equation (1) [35].

$$-J = A(B + C\cos\alpha + \cos^2\alpha)\exp(Dr) \quad (1)$$

In fact, a fit of this expression to experimental data for a series of oxido- bridged iron(III) dimers indicates that the antiferromagnetic interaction increases when α decreases or when r decreases. This correlation is independent of additional bridging ligands being present. Since for polynuclear complexes a distinct angular dependence had been observed, *Christou* et al. used the expression from Equation (1) to fit the magnetic data of a series of hexanuclear iron(III) complexes comprising mixed bridging modes including oxido, hydroxido, and alkoxido groups [36]. Based on the spin Hamiltonian defined as $\hat{H} = -J(\hat{S}_1\hat{S}_2)$, this has lead to the parameters $A = 4 \cdot 10^7 \text{ cm}^{-1}$, $B = 0.2$, $C = -1$ and $D = -0.07 \text{ pm}^{-1}$. Moreover, it was found that whenever more than one bridge is present between two iron centers, the best results are obtained by employing the average distance for the shortest Fe–O bridge, which in generally corresponds also to the one with the widest Fe–O–Fe angle.

Applying this relationship to the hexanuclear iron(III) complex **1** this results in the J values listed in Table 6, which correspond to the coupling scheme depicted in Scheme 3. This neglects in accordance with the utilized magnetostructural relationship any significant contribution via the additional diazine bridges present between the rim iron centers (Fe1, Fe2, Fe3, and Fe4) of the paddle wheel and to two iron centers (Fe5 and Fe6) at the axle. The simulated [37] temperature dependence of $\chi_{\text{M}}T$ utilizing the derived parameters is shown as solid line in Figure 3. A slightly reduced g -value of 1.79 had to be used, which is lower than

the expected value for an iron(III) high spin ($g \approx 2$), but it should be kept in mind, that the g -value is affected most by all kinds of experimental error and that paramagnetic impurities (indicated by the increase of χ_M below 10 K) as well as temperature independent paramagnetism could not be included in the simulation. Despite these constraints the simulated behavior is in good agreement with the experimental data.

As expected, all estimated $\text{Fe}_m\text{--Fe}_n$ exchange constants (J_{mn}) through the oxygen bridges are antiferromagnetic with values in the range between -11 and -45 cm^{-1} . Within the rim of the paddle wheel the exchange constants can be divided into two groups corresponds to the observed angles at the bridging oxygen atoms (cf. Table 3). The smallest couplings are assigned to the pairs Fe1–Fe2 and Fe3–Fe4 bridged by μ -OMe and μ_3 -O groups with values of $J_{12} = -11$ and $J_{34} = -13 \text{ cm}^{-1}$. Significantly larger values are attributed to the other two pairs Fe1–Fe4 and Fe2–Fe3 bridged by a μ -OMe and a μ_3 -OH group, respectively, with $J_{14} = -28$ and $J_{23} = -36 \text{ cm}^{-1}$. The largest couplings are expected for the exchange pathways between pairs consisting of an iron centers at the axel and the relevant iron centers of the rim forming the Fe_3O fragments (J_{15} , J_{25} , J_{36} , and J_{46}) with values of about -40 cm^{-1} .

This leads to a significant difference in strength between the coupling constants. The resulting spin alignments within **1** are indicated in Scheme 3. Within the trinuclear Fe_3O fragments this results in competing exchange interactions with a parallel alignment of spins along the exchange pathways Fe1–Fe2 and Fe3–Fe4, which is in contrast to the antiferromagnetic coupling between these iron centers. Similar situations of competing magnetic exchange interactions have been reported in the literature [38,39]. According to the notation of Kahn [40] the exchange pathways Fe1–Fe2 and Fe3–Fe4 can be regarded as frustrated. Due to the antiparallel alignment along the Fe1–Fe4 and Fe2–Fe3 pathways an overall $S = 0$ spin ground state results for the hexanuclear compound **1**, which is consistent with the experimental data.

Conclusions

Attempts to utilize 2,6-di(pyrazol-3-yl)pyridine (H_2 bpp) as a meridional capping ligand for trinucleating core fragments based on the triaminoguanidine ligand system failed, due to a subtle balance between the homoleptic and mononuclear species on the one hand and the desired heteroleptic trinuclear system on the other hand. Instead, under aerobic and basic conditions the $\{\text{Fe(III)bpp}\}^+$ subunits are formed, which assemble to the hexanuclear complex **1** with additional oxido, hydroxido, and methoxido bridging ligands.

Utilizing the appropriate stoichiometry, the hexanuclear iron(III) complex **1** can be deliberately synthesized in high yield as the first oligonuclear complex with H_2 bpp as a capping ligand. The paddle-wheel like structure is composed of six iron(III) ions in a distorted octahedral coordination geometry. The six iron centers can be divided into two Fe_3O fragments with a μ_3 -oxido bridge. The magnetic data suggests an overall $S = 0$ spin ground state with antiferromagnetic exchange interactions between the iron centers. A simulation confirms the assignment of the exchange constants, leading a situation with two frustrated exchange pathways, one within each of the Fe_3O fragments.

Experimental Section

Materials: The ligand 2,6-di(pyrazol-3-yl)pyridine (H_2 bpp) was synthesized according to a published procedure starting from 2,6-diacetylpyridine [16]. All other starting chemicals are commercially available and were used without further purification.

Physical Measurements: The melting point is given uncorrected and was determined with a VEB Analytik Dresden HMK 72/41555. The infrared spectra were recorded on a Bruker IFS55/EQUINOX spectrometer. Mass spectra were measured on a Bruker MAT SSQ 710 spectrometer. Elemental analyses were determined on a Leco CHNS/932 and a VARIO EL III elemental analyzer. Magnetic susceptibilities were obtained for a polycrystalline sample using a Quantum-Design MPMSR-5S SQUID magnetometer, measurements were performed with an applied magnetic field of 2000 and 5000 Oe in the temperature range from 300 to 2 K. The measured values of the molar magnetic susceptibility χ_M were corrected with respect to diamagnetic contributions.

[Fe₆(bpp)₄(μ_3 -O)₂(μ -OMe)₃(μ -OH)Cl₂] (1): The ligand H₂ bpp (160 mg, 0.8 mmol) was added in portions to a stirred solution of FeCl₂·4H₂O (226 mg, 1.1 mmol) in methanol/pyridine mixture (1:1, 15 mL). The color changed immediately from yellow to red. The reaction mixture was stirred for additional 15 min, during which period the color intensified to deep red. Slow diffusion of methanol into the reaction mixture within two weeks yields red prism of **1** · 1.5py suitable for X-ray crystallography. These were isolated, washed with methanol, and finally dried in air, upon which the crystals lose the pyridine of crystallization. (Yield: 190 mg, 70%). Mp. > 200 °C. IR (KBr): 3435 (s br, ν (OH)), 3111, 3083, 3056 (all w, ν (CH) arom.), 2918 (m, ν_{as} (CH₃)), 2814 (m, ν_s (CH₃)), 1610, 1571, 1464 (all vs, ν_{as} (C=C) arom.), 1433 (m), 1352 (vs), 1324 (w), 1157 (s), 1146 (vs), 1121 (vs), 1070 (m), 975 (m), 943 (m), 770 (vs), 666 (w), 646 (w), 547 (m br), 493 (vs br, ν (Fe-Cl)) cm⁻¹. MS (ESI⁺ DMF/MeOH) m/z 1349 (100%, [Fe₆(bpp)₄(μ_3 -O)₂(μ -OMe)₃(μ -OH)Cl]⁺), 1313 (85%, [Fe₆(bpp)₄(μ_3 -O)₂(μ -OMe)₃(μ -O)]⁺). [Fe₆(bpp)₄(μ_3 -O)₂(μ -OMe)₃(μ -OH)Cl₂], C₄₇H₃₈Cl₂Fe₆N₂₀O₆ (1384.91 g/mol): C 40.76 (calc. 41.24); H 2.77 (3.36); N 20.23 (20.67) %.

X-ray Crystallographic Studies: X-ray measurements were carried out with a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K α radiation (λ = 71.073 pm) at 183(2) K. The crystallographic data are summarized in Table 7. Data were corrected for Lorentz and polarization effects, but not for absorption effects [41–43]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares techniques against F_o^2 using SHELXL-97 [44]. The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. One of the co-crystallized pyridine molecules is located in hydrogen-bonding distance from the μ -OH group, whereas the additional 0.5 molecules are found to be orientationally disordered at a partially filled position with occupancy factors of 0.5. This position is within an hydrophobic region in the crystal structure build by the pyrazolido ligands at the axle of the paddle-wheel structure. Crystallographic data for complex **1** · 1.5 py have been deposited with the Cambridge Crystallographic Data Centre CCDC 761355. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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Scheme 1. The 2,6-di(pyrazol-3-yl)pyridine ligand (H_2 bpp).

Scheme 2. Tritopic triaminoguanidine core $[H_6L]^+$.

Scheme 3. Schematic representation of the exchange pathways through the bridging oxygen atoms. The arrows indicate alignment of the unpaired electrons of the iron centers.

Figure 1. Molecular structure of compound $[Fe_6(bpp)_4(\mu_3-O)_2(\mu-OMe)_3(\mu-OH)Cl_2]$ (**1**). The hydrogen atoms are omitted for clarity.

Figure 2. Representation of the Fe_6 core unit of compound **1**. Only the coordinating nitrogen atoms of the ligands are shown.

Figure 3. Plots of χ_M ($\circ$) and $\chi_M T$ ($\bullet$) vs. T for compound **1**. The solid line represents the simulation (for details see text).

Table 1. Selected bond lengths [pm] and angles [°] for complex **1**.

Fe1–O1	199.4(5)	Fe2–O1	203.3(5)
Fe1–O1M	198.2(5)	Fe2–O1H	194.4(5)
Fe1–O3M	198.5(5)	Fe2–O3M	198.3(5)
Fe1–N2	206.4(6)	Fe2–N7	206.4(6)
Fe1–N3	220.5(6)	Fe2–N8	220.6(6)
Fe1–N4	217.5(6)	Fe2–N9	217.5(6)
Fe3–O2	201.0(5)	Fe4–O2	203.2(5)
Fe3–O1H	193.5(5)	Fe4–O1M	196.5(5)
Fe3–O2M	199.5(5)	Fe4–O2M	196.8(5)
Fe3–N12	218.3(6)	Fe4–N17	218.8(6)
Fe3–N13	219.8(6)	Fe4–N18	219.8(6)
Fe3–N14	205.7(6)	Fe4–N19	207.5(6)
Fe5–O1	194.0(5)	Fe6–O2	192.0(5)
Fe5–N1	212.8(7)	Fe6–N5	213.3(6)
Fe5–N6	212.4(6)	Fe6–N10	210.4(6)
Fe5–N11	213.2(6)	Fe6–N15	213.0(6)
Fe5–N16	211.6(6)	Fe6–N20	212.1(6)
Fe5–Cl1	240.4(2)	Fe6–Cl2	242.6(2)
O1–Fe1–N3	154.40(22)	O1–Fe2–N8	153.44(22)
O1M–Fe1–O3M	158.02(20)	O1H–Fe2–O3M	161.11(20)
N2–Fe1–N4	143.93(23)	N7–Fe2–N9	143.75(23)
O2–Fe3–N13	153.17(21)	O2–Fe4–N18	153.66(22)
O2M–Fe3–O1H	158.34(19)	O1M–Fe4–O2M	161.88(19)
N12–Fe3–N14	144.96(22)	N17–Fe4–N19	144.15(22)
O1–Fe5–Cl1	170.73(16)	O2–Fe6–Cl2	170.92(16)
N1–Fe5–N11	174.74(23)	N5–Fe6–N15	175.73(22)
N6–Fe5–N16	174.11(23)	N10–Fe6–N20	173.30(23)

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Table 2. Fe–N–N–Fe torsion angles [°] for complex **1**.

Fe1–N2–N1–Fe5	173.8	Fe3–N12–N11–Fe5	169.6
Fe1–N4–N5–Fe6	172.7	Fe3–N14–N15–Fe6	179.6
Fe2–N7–N6–Fe5	179.4	Fe4–N17–N16–Fe5	175.6
Fe2–N9–N10–Fe6	179.9	Fe4–N19–N20–Fe6	177.9

Table 3. Fe–O–Fe bridging angles [°] for complex **1**.

Fe1–O3M–Fe2	96.3	Fe3–O2M–Fe4	97.1
Fe1–O1–Fe2	94.5	Fe3–O2–Fe4	94.5
Fe1–O1M–Fe4	110.8	Fe2–O1H–Fe3	111.9
Fe1–O1–Fe5	124.8	Fe3–O2–Fe6	124.6
Fe2–O1–Fe5	122.9	Fe4–O2–Fe6	123.7

Table 4. Interatomic Fe...Fe separations [pm] for complex **1**.

Fe1...Fe2	295.6	Fe3...Fe4	297.0
Fe1...Fe3	442.4	Fe2...Fe4	434.4
Fe1...Fe4	324.9	Fe2...Fe3	321.4
Fe1...Fe5	348.7	Fe3...Fe6	348.1
Fe1...Fe6	408.4	Fe3...Fe5	409.4
Fe2...Fe5	349.1	Fe4...Fe6	348.5
Fe2...Fe6	403.9	Fe4...Fe5	404.6
Fe5...Fe6	617.6		

Table 5. BVS^{a)} values for selected atoms in the crystal structure of **1**; values including hydrogen atoms at preset distances as used in the solution of the crystal structure are given in parentheses.

Fe1	2.93	O1	1.62
Fe2	2.93	O2	1.63
Fe3	2.98	O1M	2.02
Fe4	2.91	O2M	1.96
Fe5	2.85	O3M	1.96
Fe6	2.87	O1H	1.23(2.23)

a) $BVS = \sum_i \exp[(r_{0,i} - r_i)/B]$ with $B = 37$ pm, $r_{0,Fe-O} = 175.9$ pm, $r_{0,Fe-N} = 183.7$ pm, $r_{0,Fe-Cl} = 206.9$ pm, $r_{0,C-O} = 139.0$ pm, and $r_{0,O-H} = 95.0$ pm. Parameters are according to ref. [23].

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Table 6. Calculated J values [cm^{-1}] for pairwise Fe–Fe interactions through the oxygen bridges in complex **1** based on Equation (1).

Fe1–Fe2	-11	Fe3–Fe4	-13
Fe1–Fe4	-28	Fe2–Fe3	-36
Fe1–Fe5	-45	Fe3–Fe6	-45
Fe2–Fe5	-37	Fe4–Fe6	-41

Table 7. Crystallographic data and structure-refinement parameters for complex **1**.

Complex	1 ·1.5 py
Empirical formula	C _{54.5} H _{45.5} Cl ₂ Fe ₆ N _{21.5} O ₆
Formula weight	1503.62
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> (pm)	1192.71(4)
<i>b</i> (pm)	2262.81(6)
<i>c</i> (pm)	1223.15(4)
α (°)	90
β (°)	113.7820(10)
γ (°)	90
<i>V</i> (nm ³)	3.02082(16)
<i>Z</i>	2
Crystal size (mm)	0.6 x 0.6 x 0.6
<i>D</i> _{calcd} (Mg m ⁻³)	1.653
μ (mm ⁻¹)	1.560
θ Range of data collection (°)	1.87, 27.49
Measured reflections	21096
Unique reflections/ <i>R</i> _{int}	13570/0.0504
Goodness-of-fit on <i>F</i> ²	1.031
Flack parameter	0.00(2)
<i>R</i> indices (all data) ^{a)}	<i>R</i> ₁ = 0.0984, <i>wR</i> ₂ = 0.1445
Final <i>R</i> indices [<i>F</i> > 2σ(<i>F</i>)] ^{a)}	<i>R</i> ₁ = 0.0600, <i>wR</i> ₂ = 0.1271

a) $R_1 = \sum (||F_o| - |F_c||) / \sum |F_o|$, $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{\frac{1}{2}}$.

The 2,6-di(pyrazol-3-yl)pyridine ligand
(H₂bpp).
44x22mm (600 x 600 DPI)

Tritopic triaminoguanidine core $[H_6L]^+$.
53x59mm (600 x 600 DPI)

Schematic representation of the exchange pathways through the bridging oxygen atoms. The arrows indicate alignment of the unpaired electrons of the iron centers.
69x58mm (600 x 600 DPI)

Molecular structure of compound $[\text{Fe}_6(\text{bpp})_4(\mu_3\text{-O})_2(\mu\text{-OMe})_3(\mu\text{-OH})\text{Cl}_2]$ (**1**). The hydrogen atoms are omitted for clarity.
168x160mm (600 x 600 DPI)

Representation of the Fe₆ core unit of compound **1**. Only the coordinating nitrogen atoms of the ligands are shown.
158x159mm (600 x 600 DPI)

Plots of χ_M ($\circ$) and $\chi_M T$ ($\bullet$) vs. T for compound **1**. The solid line represents the simulation (for details see text).
150x105mm (600 x 600 DPI)