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Synthesis and transition metal coordination chemistry of a novel hexadentate bispidine ligand[†]

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Reported is the new bispidine-derived hexadentate ligand L (L = 3-(2-methylpyridyl)-7-(bis-2-methylpyridyl)-3,7-diazabicyclo[3.3.1]nonane) with two tertiary amine and four pyridine donor groups. This ligand can form heterodinuclear and mononuclear complexes and, in the mononuclear compounds discussed here, the ligand may coordinate as a pentadentate ligand, with one of the bispyridinemethane-based pyridine groups un- or semi-coordinated, or as a hexadentate ligand, leading to a pentagonal pyramidal coordination geometry or, with an additional monodentate ligand, to a heptacoordinate pentagonal bipyramidal structure. The solution and solid state data presented here indicate that, with the relatively small Cu^{II} and high-spin Fe^{II} ions the fourth pyridine group is only semi-coordinated for steric reasons and, with the larger high-spin Mn^{III} ion genuine heptacoordination is observed but with a relatively large distortion in the pentagonal equatorial plane.

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Introduction

The 3,7-diaza-bicyclo[3.3.1]nonane (bispidine) motif offers a rigid ligand backbone, resulting in a high degree of preorganization and rigidity, combined with a wide synthetic variability for tailor-made ligand systems. The bispidine itself was first discovered by Mannich and Mohs¹ and appears as a substructure of the natural product sparteine. The general synthesis of bispidines involves two consecutive double Mannich reactions via the piperidone intermediate.¹ Based on the possibility to enforce specific coordination geometries and therefore stabilize complexes with specific properties,^{2,3} the bispidine transition metal coordination chemistry has developed into a particularly broad field, with applications in catalytic sulfoxidation7-9 aziridination,⁴⁻⁶ and C-H-activation processes,^{10–12} molecular magnetism,^{13–16} the development of new ionophores,17 radiotracers for positron emission tomography (PET),¹⁸⁻²⁰ and copper sensors.^{21,22} Typical bispidine ligands and the main structural features of their transition metal complexes are shown in Chart 1.

Here, we present the new bispine ligand L with a bis(2pyridyl)methyl substituent, leading to a hexadentate ligand, an isomer of the known hexadentate bispidine L^2 , with strikingly different complexing properties: this ligand can either coordinate to a single metal ion, leading to a pentagonal pyramidal structure and possibly to heptacoordination, when a monodentate ligand completes the distorted pentagonal bipyramidal coordination sphere, or behave as a dinucleating ligand (see Chart 1). We discuss two different synthesis strategies for the ligand - the classical double Mannich reaction sequence and the alkylation of the secondary amine at N7 of the tetradentate bispidone precursor. Also, in order to suppress retro Mannich ligand decay and hence enhance the stability of the formed complexes, ligand L was reduced at C9 to produce the corresponding alcohol derivative LOH. Here, we report the first row transition metal coordination chemistry of the new bispidines as mononucleating ligands, and in particular we discuss the solid state and solution structures based on X-ray crystallography, electrochemistry and EPR as well as ligand field spectroscopy.

Results and discussion

Ligand synthesis

The typical procedure to build up a bispidone is by two consecutive double Mannich reactions. The precursor for the synthesis of the desired ligand L, the known di(2-pyridyl)amine (2), is obtained in a two-step procedure from the commercially available di(2-pyridyl)ketone.²³ This was reacted with the common Npy₂ piperidone (pL) to obtain L in up to 16% yield (Scheme 1). Due to the modest yield, L was alternatively obtained by alkylation of the secondary amine N7 of the bispidine precursor with the halogenated dipyridyl building block (Scheme 1). For this convergent synthesis, we decided to insert

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Chart 1 Ligands discussed in this publication, and the two isomeric hexacoordinate structures with L^2 and L (if X = void), as well as the two coordination modes (mono- and dinucleating) of the hexadentate bispidine L.

a latent benzyl protecting group at N7 by choosing benzyl amine as the amine component in the second Mannich reaction.¹⁷ The resulting benzylated bispidine (5) was hydrogenated with palladium on activated charcoal, to remove the benzyl group and yield the secondary amine precursor (6). The di(2-pyridyl)methyl chloride (4) was obtained by a slightly modified published procedure,²⁴ where the di(2-pyridyl)ketone was reduced to the corresponding alcohol (3) with sodium borohydride and subjected to an Apple reaction, to obtain the di(2-pyridyl)methyl chloride (4). After refluxing the bispidine precursor (6) with the chloride (4) in acetonitrile with sodium carbonate as base and a catalytic amount of sodium iodide, the desired ligand L was obtained in yields up to 53%, *i.e.* this procedure is clearly more efficient than the double Mannich reaction. Reduction of the ketone L at C9 to the corresponding alcohol L^{OH} with sodium borohydride, to prevent the retro Mannich reaction, resulting in ligand decomposition under acidic (pH < 3) or alkaline conditions (pH > 10), produced (L^{OH}) in 93% yield (Scheme 2).

Transition metal coordination chemistry

All syntheses were carried out under ambient conditions in methanol, if not mentioned otherwise. Equimolar solutions of the ligand and the metal salt were combined and stirred at room temperature overnight. Suitable crystals for X-ray crystal structure determination were obtained by diffusion of diethylether into the methanolic complex solutions.

Copper complexes. In the structures of the Cu^{II} complexes $[Cu^{II}(L)]^{2+}$ and $[Cu^{II}(L^{OH})]^{2+}$, shown in Fig. 1 (selected structural data presented in Table 1), only five donors of the hexadentate ligands are coordinated (in both cases, a fluorine atom of the tetrafluoroborate counterion is interacting with Cu^{II} at the open position *trans* to N7 with a Cu–F distance of approx. 2.6 Å, see Table 1). One of the two pyridine groups attached to N7 (py4) is dangling, similar to the phenyl group in the analogous pentadentate ligand L^3 (see Chart 1), from which structures of hexacoordinate Fe^{II} complexes similar to those in Fig. 1 – with one monodentate ligand trans to N7 – are



Scheme 1 Two different synthetic routes to ligand L.



Scheme 2 Reduction of L to L^{OH}.

known.²⁵ That is, the coordination geometry around Cu^{II} is comparable to that observed with L^1 (see Table 1).^{4,26,27} However, the dangling pyridine donor py4 of L and L^{OH} clearly points in the direction of the Cu^{II} center with a $Cu \cdots N$ distance of 3.89 Å and 3.85 Å (L and L^{OH} , respectively), which is an important difference to the structure of the Fe^{II} complex with $L^{3,25}$ The third pyridine donor py3 is coordinated *trans* to N3, and this defines the pseudo-Jahn–Teller axis along Cu–N7. Since the second apical position is unoccupied in contrast to the structures with L^1 , the Cu–N7 distances are as expected



Fig. 1 ORTEP plots of $[Cu^{II}(L)]^{2+}$ (left) and $[Cu^{II}(L^{OH})]^{2+}$ (right), hydrogen atoms are omitted for clarity, ellipsoids are shown with 50% probability.

| | $[Cu^{II}(L)]^{2^+}$ | $[Cu^{\rm II}\!(\rm L^{OH})]^{2^+}$ | $\left[Cu^{II}\!\left(L^1\right)\!Cl\right]^{\!+}$ | $[\mathrm{Cu}(\mathrm{L}^2)]^{2+}$ |
|---------------|----------------------|-------------------------------------|--|------------------------------------|
| Distances [Å] | | | | |
| Cu–N3 | 2.003(3) | 1.993(2) | 2.036(2) | 2.087(3) |
| Cu-N7 | 2.237(3) | 2.233(2) | 2.368(2) | 2.045(3) |
| Cu-py1 | 2.047(3) | 2.052(2) | 2.028(2) | 2.573(3) |
| Cu-py2 | 2.040(3) | 2.039(2) | 2.029(2) | 2.208(3) |
| Cu-py3 | 1.984(3) | 1.976(2) | 2.029(2) | 2.028(3) |
| Cu-py4 | 3.893(3) | 3.854(2) | _ () | 2.009(3) |
| Cu-F11 | 2.637(3) | 2.653(2) | _ | _ `` |
| N3…N7 | 2.934(5) | 2.930(3) | 2.915 | 2.83 |
| py1…py2 | 3.986(5) | 3.994(3) | 3.995 | 4.67 |
| Angles [°] | | | | |
| N3-Cu-N7 | 87.41(13) | 87.57(8) | 82.53(6) | 86.43(12) |
| N3-Cu-py1 | 80.89(14) | 80.84(9) | 81.39(7) | _ |
| N3-Cu-py2 | 80.73(14) | 80.79(9) | 80.94(7) | _ |
| N3-Cu-py3 | 168.79(14) | 169.18(9) | 160.82(7) | 154.39(13 |
| N7-Cu-py1 | 104.53(14) | 103.72(8) | 88.32(6) | _ ` |
| N7-Cu-py2 | 91.97(12) | 92.52(8) | 98.43(6) | _ |
| py1-Cu-py2 | 154.62(13) | 154.84(9) | 160.07(7) | 148.53 |
| N7-Cu-py3 | 82.81(12) | 83.11(8) | 79.27(7) | — |
| py1-Cu-py3 | 96.2(1) | 96.02(9) | 110.00(6) | |
| py2-Cu-py3 | 105.0(1) | 105.02(9) | 97.02(6) | |
| | | | | |

Table 1 Selected distances and angles of the Cu^{II} complexes of L and L^{OH} in comparison with those of L^1 and L^2 (ref. 4 and 28)

comparably short (see Table 1) - the pseudo-Jahn-Teller axis of the complex with the hexadentate isomer of L, L^2 (also presented in Table 1), is oriented along the py1-Cu-py2 axis. Interestingly, the position of the py3 donor in $[Cu^{II}(L)]^{2+}$ and $[Cu^{II}(L^{OH})]^{2+}$ is significantly different to that in $[Cu^{II}(L^{1})Cl]^{+}$, with a shorter Cu-N distance (1.98 Å, 1.98 Å vs. 2.03 Å) and a compressed py1-Cu-py3 angle (96.2°, 96.0°, vs. 110.0°). Together with the significant tilt of the Cu-N7 axis with respect to the CuN₄ plane (increase of the py1-Cu-N7 angle of approx. 15°), this indicates that the particular distortion may be due to the Cu---py4 interaction and that the pentagonalpyramidal coordination geometry (hexacoordination of L and $\boldsymbol{L^{OH}}$) is prevented by ligand-induced strain (crowding in the basal plane due to relatively short metal-donor distances), *i.e.*, a larger metal ion could lead to the desired coordination geometry.

The redox potentials and electronic properties of the new complexes and of selected reference compounds are listed in Table 2. It appears that as a whole, the solution properties are very similar to those of the L^1 -based Cu^{II} complex and therefore, we conclude that the solution structure is similar to that in the solid (see Fig. 1), *i.e.* square pyramidal (or pseudo-octahedral) with a dangling but weakly interacting py4. This is supported by the axial EPR spectrum (see Fig. 2) and the spin

Table 2 Redox potentials (MeCN vs. Fc/Fc⁺, vs. Ag/AgNO₃; H₂O vs. K₃[Fe(CN)₆]^a or vs. Ag/AgCl^b) and spectroscopic data of the Cu^{II} complexes of L and L^{OH}, in comparison with other Cu^{II} bispidine complexes^{2,28,30,44}

| | Cu ^I /Cu ^{II} [mV] | | dd Cu ^{II} [nm] | | |
|-----------------------------|--|----------------------|---|---|--|
| | MeCN | H ₂ O | MeOH (ε [M ⁻¹ cm ⁻¹]) | EPR $(g_{x,y}, g_z; A_{x,y}, A_z)$ MeOH–EtOH, 5K A in 10 ⁻⁴ cm ⁻¹ , SOPHE simulation ^{45,46} | |
| $[Cu(L)](BF_4)_2$ | -651 (-602) | $-786^{a}; -515^{b}$ | 626 (119) | 2.061, 2.237; 8.5, 172.9 | |
| $[Cu(L^{OH})](BF_4)_2$ | -671 (-538) | $-730^{a}; -459^{b}$ | 630 (112) | | |
| $[Cu(L)](ClO_4)_2$ | -678 (-594) | — | _ | _ | |
| $[Cu(L^1)]^{2+}$ | -776 (-603) | -523^{b} | 617 (108) | 2.060, 2.217; -178 | |
| $[Cu(L^2)]^{2+}$ | -745 (-573) | -502^{b} | 620 (125) | 2.069, 2.208; -169 | |
| $\left[Cu(L^3)\right]^{2+}$ | _ | -433^{b} | 573 | _ | |



Fig. 2 X-band EPR spectrum of $[Cu^{II}(L)]^{2+}$ in MeOH–EtOH (9 : 1) at 5 K and 9.423336 GHz, black line (bottom): experimental spectrum, red line (top) simulated spectrum.

Hamiltonian parameters. As expected, the ligand field of the Cu^{II} complex is slightly reduced by reduction of the ligand from L to L^{OH} , and the redox potentials are consequently more positive (destabilization of the Cu^{II} state).²⁹ More importantly, the ligand field exerted by L is significantly smaller than that of L^1 , and the corresponding redox potentials therefore are less negative, *i.e.* Cu^{II} is less stabilized by L than by L^1 . This is in agreement with the structural properties enforced by L, *i.e.* the weak interaction of py4 leads to a distortion of the pseudo-square pyramidal coordination geometry.

Due to the fact that the stability constants of Cu^{II} complexes vary over a wide range and those of Cu^I are much less variable, there is an approximate linear correlation between Cu^{II/I} redox potentials and the corresponding Cu^{II} stability constants.³¹ For ligands with a similar organic backbone and a constant donor set, this type of correlation offers an ideal possibility for an accurate prediction of stability constants and, for the very rigid bispidine scaffold it has been demonstrated that this is the case.^{30,32} Based on these established correlations and the redox potentials reported in Table 2, the expected stability constants for the two complexes are log K- ${[Cu^{II}(L)]^{2+}} = 16.0 \text{ and } \log K {[Cu^{II}(L^{OH})]^{2+}} = 16.3 \text{ (see ESI}^{\dagger}). \text{ As}$ discussed above, these values are comparable but slightly smaller than the experimentally determined value for $[Cu^{II}(L^1)]^{2+}$, and we believe that this is due to the distortion induced by semi-coordination of py4.

Iron complexes. Most of the reported Fe^{II} bispidine complexes exist in the *S* = 2 spin state (high spin), most are close to the spin crossover limit, and only one genuine low spin (*S* = 0) complex has been reported so far;^{29,33,34} intermediate spin (*S* = 1) electronic configuration is extremely rare for Fe^{II} and may be imposed by a pentagonal bipyramidal coordination geometry. The generally larger metal donor distances with high spin Fe^{II} compared to Cu^{II} (approx. 2.2 *vs.* 2.0 Å for amine

donors) leads to the expectation that L might enforce sevencoordination and a distorted pentagonal bipyramidal geometry with Fe^{II}. From the two crystal structures of the $[Fe^{II}(L)X]^{n+}$ complexes (X = Cl, OHMe, see Fig. 3 and Table 3) obtained, it emerges, however, that the fourth in-plane pyridine donor (py4), similar to the Cu^{II} structures discussed above, is dangling but with an even shorter distance to the metal center (3.03 Å *vs.* 3.85 Å) and therefore may be considered semi-coordinated. Also presented in Fig. 3 and Table 3 is an Fe^{III} complex of L, obtained by reaction of the ligand with an Fe^{II} salt under ambient conditions – all other complexation reactions were performed under inert atmosphere. For comparison, selected structural data of other iron-amine/pyridine complexes are also listed in Table 3.

In the structures of the Fe^{II} complexes of L and L^{OH} , an octahedral coordination geometry is completed by a monodentate Cl⁻ or methanol solvent molecule, respectively, coordinated trans to N7. Semi-coordination of py4 again leads to a distortion of the remaining Fe^{II}-N₂py₃X chromophore, similar to but more pronounced as that discussed above for the Cu^{II} complexes, in particular for the unreduced L-based system (reduction of the ketone leads to a slight increase of the donor strength; the discussion refers to the ketone-based ligand L): $^{27-29}$ (i) the data in Table 3 suggest that the Fe…py4 interaction tends to reduce the Fe-N7 distance (and concomitantly increases the Fe–N3 distance);^{28,30} (ii) the Fe…py4 interactions leads to an asymmetry with respect to the coordination of the two pyridine donors py1 and py2, i.e., the two angles py1,2-Fe-py3 are strikingly different (85° vs. 137° and 87° vs. 130°, respectively).

Due to problems with the solubility of the various complexes, the redox potentials (see Table 4) could not all be determined in the same solvent, and the electronic spectra in solution (also given in Table 4) are, as expected for high spin Fe^{II} systems, relatively feature-less and therefore not fully assigned. Qualitatively, it appears however, that there is a significant difference between the solution properties of the complexes with L and L^{OH} in comparison to the complexes of the analogues L^1 , L^2 and L^3 , suggesting also a semi-coordination of the additional pyridine group py4. Specifically, there is the expected reduction of the ligand field and a concomitant destabilization of the reduced Fe^{II} form.

Interestingly, when the complex synthesis is performed under ambient atmosphere, spontaneous oxidation of the Fe^{II} complex to Fe^{III} takes place,³⁷ and the corresponding complex could be isolated and crystallized; the structure of the molecular cation is also shown in Fig. 3 and selected structural parameters are given in Table 3 together with those of a similar published structure with another pentadentate bispidine ligand $L^{1'}$ ($L^{1'}$ is an isomer to L^1 with the pyridine group attached to N3 instead of N7). The complex has the expected distorted octahedral geometry with L coordinated as a tetradentate ligand to a high spin Fe^{III} center with a semicoordinated py4 donor. The metal donor distances are very similar to those of the corresponding high spin Fe^{II} complex (see Table 3) but, as in the similar $L^{1'}$ based system, the OMe⁻



Fig. 3 ORTEP plots of the complex cations (a) [Fe^{II}(L)OHMe]²⁺, (b) [Fe^{II}(L^{OH})Cl]⁺, and (c) [Fe^{III}(L)OMe]²⁺; hydrogen atoms are omitted for clarity, ellipsoids are shown with 50% probability.

donor, coordinated as an anionic coligand has, as expected, a relatively short metal-ligand bond (Fe^{III}–O = 1.79 Å). Other Fe^{III} methoxy complexes with similar amine/pyridine ligands (*e.g.* N4py = *N*,*N*-bis(2-pyridyl)methyl)-*N*-(bis-2-pyridylmethyl)-amine³⁹ and bztpen = *N*-benzyl-*N*,*N'*,*N'*-tris(2-methylpyridyl)ethylendiamine)⁴⁰ have similar structural features, especially also with respect to the Fe–O–CH₃ angle of 149°, which is typical for a high spin Fe^{III} electronic configuration:^{33,34,39,40} typical Fe–O–CH₃ angles for low spin Fe^{III} are around 130°, those for high spin Fe^{III} are around 150–170°.^{38,39}

Confirmation of the electronic ground state in solution arises from magnetic moment determinations (Evans-NMR, CD₃CN). For the two high spin Fe^{II} complexes, the effective magnetic moments are: $\mu_{eff} = 4.9612$ B.M. for [Fe^{II}(L)OHMe]²⁺ and $\mu_{eff} = 4.8734$ B.M. for [Fe^{II}(L^{OH})Cl]⁺, and this is typical for high spin d⁶ configuration, with S = 2 and a spin only moment of $\mu_{eff} = 4.899$ B.M. The magnetic moment of [Fe^{III}(L)OMe]²⁺ in solution is $\mu_{eff} = 5.1882$ B.M., typical for a high spin d⁵ (S = 1)

5/2) electronic ground state with a spin only moment of $\mu_{\rm eff}$ = 5.916 B.M.

Manganese complexes. There are a number of Mn^{II} bispidine complexes known, especially with tetradentate bispidine ligands and, as expected for high spin d⁵ systems, their geometries are generally octahedral with Mn-N distances significantly larger than those of the Fe^{II} complexes.^{27,29,41} Therefore and since heptacoordinate Mn^{II} complexes (pentagonal bipyramidal and monocapped trigonal prismatic) are not uncommon,42-44 the hexacoordinating bispidine L was coordinated to Mn^{II}. Diffusion of diethylether into the methanolic solution of [Mn^{II}(L)Cl]⁺, obtained by the combination of a methanolic solution of MnCl₂ with an equimolar amount of ligand, produced practically colorless needles, suitable for X-ray diffraction. A plot of the molecular cation of $[Mn^{II}(L)Cl]^+$, obtained by X-ray crystal structure analysis, is shown in Fig. 4; selected structural parameters are presented in Table 5, which also lists relevant data for comparison (there are two indepen-

Table 3 Selected bond distances and angles of the Fe^{III} and Fe^{III} complexes of L, L^{OH} and other bispidine ligands

| | $[Fe^{II}(L)-OHMe]^{2+}$ | $[\mathrm{Fe}^{\mathrm{II}}(\mathrm{L}^{\mathrm{OH}})\mathrm{Cl}]^{+}$ | [Fe ^{II} (L ¹)OHMe] ²⁺ (ref. 41) | $[Fe^{II}(L^1)Cl]^+$ (ref. 33) | $[Fe^{II}(L^2)-SO_4]^{33}$ | $[Fe^{II}(L^3)Cl]^+$ (ref. 25) | $\left[\mathrm{Fe}^{\mathrm{III}}(\mathrm{L})-\mathrm{OMe} ight]^{2^+}$ | [Fe ^{III} (L ^{1'})OCH ₂ CF ₃] ^{2+ o} (ref. 36) |
|----------------------|--------------------------|--|---|--------------------------------|----------------------------|--------------------------------|---|--|
| Distances [Å] | | | | | | | | |
| Fe-N3 | 2.289(2) | 2.235(2) | 2.177(3) | 2.194(2) | 2.215(9) | 2.213(2) | 2.1916(15) | 2.202(2) |
| Fe-N7 | 2.2482(18) | 2.309(2) | 2.293(3) | 2.362(2) | 2.274(10) | 2.342(2) | 2.2951(15) | 2.193(2) |
| Fe-py1 | 2.265(2) | 2.294(2) | 2.163(3) | 2.182(2) | 2.206(10) | 2.232(2) | 2.2281(17) | 2.106(2) |
| Fe-py2 | 2.184(2) | 2.189(2) | 2.231(3) | 2.142(2) | 2.172(10) | 2.173(2) | 2.1425(16) | 2.095(2) |
| Fe-py3 | 2.209(2) | 2.174(2) | 2.110(3) | 2.134(2) | 2.195(10) | 2.143(2) | 2.1099(16) | 2.093(2) |
| Fe-py4 | 3.025(1) | 3.352(3) | | | 1.957(8) | $4.058(3)^{a}$ | 3.240(2) | — |
| Fe-X _A | $2.0939(19)^{b}$ | $2.3954(7)^{b}$ | $2.120(3)^{b}$ | $2.416(1)^{o}$ | $1.957(8)^{c}$ | $2.3616(7)^{b}$ | $1.7923(14)^{b}$ | $1.791(2)^{c}$ |
| N3…N7 | 2.897(6) | 2.908(6) | 2.923 | 2.879(2) | 2.883(9 | 2.938(3) | 2.861(2) | 2.893(3) |
| py1…py2 | 4.150(6) | 4.260(6) | | 4.195(2) | 4.245(10) | 4.265(3) | 4.177(2) | 4.090(3) |
| Angles [°] | | | | | | | | |
| N3-Fe-N7 | 79.50(7) | 79.44(7) | 81.6(1) | 78.27(5) | 79.94(3) | 80.29(7) | 79.19(6) | 82.33(7) |
| N3-Fe-py1 | 70.92(7) | 72.56(8) | 77.0(1) | 76.00(5) | 76.32(3) | 76.07(8) | 73.59(6) | |
| N3-Fe-py2 | 72.05(7) | 73.59(8) | 76.5(1) | 76.48(6) | 76.01(3) | 75.35(8) | 74.18(6) | |
| N7-Fe-py1 | 99.06(7) | 97.21(8) | | 94.12(5) | 89.18(3) | 87.21(7) | 95.66(6) | |
| N7-Fe-py2 | 93.61(7) | 89.51(8) | | 86.15(5) | 91.75(3) | 92.41(7) | 89.48(6) | |
| py1-Fe-py2 | 137.70(7) | 143.54(8) | | 151.82(6) | 151.70(4) | 151.05(8) | 145.73(5) | 153.64(8) |
| py1–Fe–py3 | 84.87(8) | 86.56(8) | | 93.68(6) | 92.1(4) | 92.18(8) | 86.85(6) | |
| ру2-Fe-ру3 | 137.41(8) | 129.70(9) | | 113.73(6) | 77.1(4) | 115.83(8) | 127.20(6) | |
| Fe-O-CH ₃ | 130.97(18) | — | — | _ | — | _ | 149.12(12) | |

 ${}^{a}L^{1'}$ is an isomer to L^{1} with the pyridine group attached to N3 instead of N7. b trans zu N7. c trans zu N3. d C-atom of the phenylring pointing in direction of the metal center.

Table 4 Redox potentials (MeCN vs. Fc/Fc^{+a}; vs. Ag/AgNO₃^b; H₂O vs. K₃[Fe(CN)₆]^c; vs. Ag/AgCl^b) and spectroscopic data of the Fe^{II} complexes of L and L^{OH}, in comparison with other Fe^{II} bispidine complexes^{33,35,36}

| | | Fe^{III}/Fe^{II} [mV] | | dd Fe ^{II} [nm] | |
|---|------------------------|--------------------------|----------------------|--------------------------|--|
| | H_2O^a | MeOH ^b | MeCN | MeCN | |
| [Fe(L)OHMe] ²⁺ | 474 | | _ | 364 | |
| [Fe(L ^{OH})Cl] ⁺ | 225 | | 222^{c} | 341, 412 | |
| [Fe(L ¹)Cl] ^{2[‡]} | _ | 156 | _ | 309; 402 | |
| $[Fe(L^2)]^{2+1}$ | _ | _ | 661^{b} | 376; 402; 457; 564 | |
| $[Fe(L^3)OTf]^+$ | — | | 773 ^c | _ | |
| ^{<i>a</i>} ν s. K ₂ [Fe(CN) _c]. | ^b vs. Ag/Ag | NO2. ^c vs. Fc | $/\mathrm{Fc}^{+}$. | | |

dent complex cations, in the unit cell, and the parameters of both are tabulated).

As hoped for, the structure of $[Mn^{II}(L)(Cl)]^+$ is heptacoordinated with the hexacoordinating bispidine and a Cl⁻ completing the distorted pentagonal bipyramidal coordination sphere. In terms of the coordination of the two dipyridinamine-based pyridine donors py3 and py4, the structure is, due to ligandenforced strain, still significantly distorted but the longer Mnpv3,4 distances of 2.34, 2.4, 2.53 and 2.65 Å all can be considered as genuine bonds. The trans angle N7-Mn-Cl of 165° (167°) is in agreement with a (distorted) bipyramidal structure. The intra-donor angles in the pentagonal plane indicate a relatively symmetrical distribution with an ideal value of 72° and an observed distribution between 67° and 82°, and the average deviation of 0.38 Å from a mean plane is significant but not very large. The most extensive distortion is related to the position of N3 (rigid N3-Mn-N7 angle) and the two pyridine groups py3 and py4 (tight and rigid chelate rings involving N7

and py3, py4), and this results in N3, py3, py4 all being above the mean equatorial plane (0.57 Å, 0.06 Å, 0.19 Å, respectively, all for molecule 1; Mn is by 0.38 Å above the plane; py1 and py2 are by 0.49 Å and 0.35 Å below the plane; the corresponding values for molecule 2 are similar, see ESI†). As a result, the repulsion between the pyridyl groups py3 (and py4) and the α hydrogen atoms of py1 (and py2) is reduced. In order to visualize the similarity between the 7-coordinated Mn^{II} and the 6-coordinated Fe^{II} structures and to justify the "semi-coordination" of py4 in the Fe^{II} and Cu^{II} structures, an overlay plot of $[Mn^{II}(L)(Cl)]^+$ and $[Fe^{II}(L)(HOMe)]^{2+}$ is also shown in Fig. 4.

The redox potential $(Mn^{II/III} \text{ couple } \nu s. \text{ SCE})$ of $[Mn^{II}(L)(Cl)]^+$ is significantly more positive than that of the hexacoordinate $[Mn(tpen)Cl]^+$ with a similar donor set, indicating that the extra pyridine donor prevents oxidation and concomitant compression of the coordination sphere. For the 7-coordinated EDTA and NOTA complexes with H₂O as an extra ligand, steric effects are of lesser importance (possible dissociation of the 7th ligand and reduction of the coordination number) and the carboxylates obviously stabilize the oxidized form (Table 6).

Squid magnetometry was used to analyze the electronic ground state of $[Mn^{II}(L)(Cl)]_2[MnCl_4]$ (Fig. 5). It follows that zero field splitting is neglectable and the magnetic susceptibility at room temperature per $[Mn^{II}(L)(Cl)]^+$ cation (S = 5/2 for the $[MnCl_4]^{2-}$ complex ion)⁴⁵ is 4.168 cm³ K mol⁻¹, typical for a high spin d⁵ center (S = 5/2, 4.337 cm³ K mol⁻¹ for g = 2). It appears that spin pairing to result in possible S = 3/2 (intermediate spin) and S = 1/2 (low spin) states, due to (distorted) pentagonal bipyramidal coordination geometry, is prevented by the long metal-donor distances and the resulting relatively weak ligand field.



Fig. 4 (a) ORTEP plot of the complex cation $[Mn^{II}(L)(Cl)]^+$ (only one of the two independent molecules is shown, hydrogen atoms are omitted for clarity, ellipsoids are shown with 50% probability); (b) overlay plot of $[Mn^{II}(L)(Cl)]^+$ (red, $M = Mn^{II}$) and $[Fe^{II}(L)(HOMe)]^{2+}$ (green, $M = Fe^{II}$).

Conclusion

The hexadentate bispidine ligands \mathbf{L} and \mathbf{L}^{OH} have been shown to be able to form heptacoordinated pentagonal bipyramidal structures. For the relatively small Cu^{II} and high spin Fe^{II} ions the fourth pyridine group is only semi-coordinated for steric reasons and, with the larger high spin Mn^{II} ion genuine heptacoordination is observed but with a relatively large distortion in the pentagonal equatorial plane. It appears that an elongation of chelate rings involving the dipyridylamine group might lead to the desired enforcement of pentagonal (bi)pyramidal structures, even for smaller metal ions, and this also emerges from similar effects observed with 6- vs. 5-membered chelate rings involving the N7-appended pyridine donor in L¹-based pentadentate bispidine ligands.46,47 Moreover, an expansion of the linker between N7 and the pyridine donors py3 and py4 would also lead to less distortion in the equatorial plane, even with relatively large metal-donor distances.

| Table 5 | Selected | structural | parameters | of | [Mn ^{II} (L)Cl] ⁺ | and | relevant |
|------------|-----------|------------|------------|----|---------------------------------------|-----|----------|
| data for o | compariso | n | | | | | |

| | [Mn ^{II} (L)Cl] | + a | $[Mn^{II}(L^1)Cl]^+$ (ref. 41) | $[Mn^{II}(tpen)-Cl]^{+b}$ |
|-------------------------------|--------------------------|-------------------------|-----------------------------------|---------------------------|
| Distance [Å] | | | | |
| Mn-N3 | 2.435(2) | 2.485(2) | 2.2829(1) | 2.485(2) |
| Mn-N7 | 2.326(2) | 2.344(2) | 2.4151(1) | 2.444(2) |
| Mn-py1 | 2.307(2) | 2.362(2) | 2.2714(1) | 2.262(2) |
| Mn-py2 | 2.389(2) | 2.342(2) | 2.2622(1) | 2.490(2) |
| Mn-py3 | 2.346(2) | 2.415(2) | 2.1910 | 2.297(2) |
| Mn-py4 | 2.647(2) | 2.529(2) | _ | 2.498(2) |
| Mn-Cl | 2.3933(8) | 2.4064(8) | 2.3914(1)(2) | 2.4544(7) |
| N3…N7 | 2.926(3) | 2.926(3) | 2.943 | _ () |
| py1…py2 | 4.273(3) | 4.246(3) | _ | — |
| Angle [°] | | | | |
| N3-Mn-N7 | 75.80(7) | 74.51(6) | 77.507(2) | _ |
| N3-Mn-pv1 | 68.29(7) | 66.82(7) | 73.599(2) | _ |
| N3-Mn-pv2 | 67.51(7) | 66.81(7) | 74.010(2) | _ |
| N3-Mn-py3 | 133.62(7) | 132.42(7) | 149.085(2) | _ |
| N3-Mn-pv4 | 127.55(7) | 127.15(7) | _ () | _ |
| N7-Mn-pv1 | 93.98(7) | 92.24(7) | _ | _ |
| N7-Mn-py2 | 94.85(7) | 94.95(7) | 85.5(1) | _ |
| N7-Mn-py4 | 69.62(7) | 70.63(7) | _ | _ |
| N7-Mn-py3 | 73.15(7) | 73.16(7) | _ | _ |
| py1-Mn-py2 | 131.00(8) | 129.00(7) | 144.4(1) | _ |
| N7-Mn-Cl | 164.62(6) | 166.62(7) | 112.147(1) | 139.44(6) |
| py1-Mn-py4 | 75.98(8) | 80.55(8) | | |
| py3-Mn-py4 | 70.56(7) | 71.45(8) | | |
| py2-Mn-py3 | 81.76(8) | 77.93(8) | | |
| ^{<i>a</i>} Two indep | endent mo | lecules. ^b t | pen = N, N, N | N'-tetrakis(2- |

^a Two independent molecules. ^b tp pyridylmethyl)ethylene-1,2-diamine.⁶⁸

Table 6 Redox potentials of $\left[Mn(L)Cl \right]^+$ and relevant data for comparison in MeCN, vs. SCE

| | $\mathrm{Mn}^{\mathrm{II/III}}\left[\mathrm{mV} ight]$ |
|--|--|
| $\begin{bmatrix} Mn(L)Cl \end{bmatrix}^+ \\ Mn(L'')Cl_2 \end{bmatrix}^a \\ \begin{bmatrix} Mn(tpen)Cl \end{bmatrix}^+ {}^b \\ \begin{bmatrix} Mn(NOTA) \end{bmatrix}^- {}^c \\ \begin{bmatrix} Mn(NOTA) \end{bmatrix}^{2-c} \\ \begin{bmatrix} Mn(EDTA) \end{bmatrix}^{2-c} \end{bmatrix}^2$ | 1171^d 911 ^a 1050 496 ^e 566 ^e |
| | |

^{*a*} L" is a tetradentate bispidine derivative;⁶⁹ $E(Ag/AgNO_3) = 343 \text{ mV } vs.$ SCE.⁷⁰ ^{*b*} tpen = N,N,N',N'-tetrakis(2-pyridylmethyl)ethylene-1,2-diamine.⁶⁸ ^{*c*} NOTA = 1,4,7-triacetato-1,4,7-triazanonane; EDTA = N,N,N',N'-tetraacetatoethylene-1,2-diamine.⁷¹ $d E(Fc/Fc^+) = 380 \text{ mV } vs.$ SCE.⁷⁰ e E(SHE) = -244 vs. SCE.⁷⁰

Experimental section

All chemicals were purchased from Sigma Aldrich and Acros. Analytical grade solvents were used without further purification and all reactions were carried out under air if not mentioned otherwise. The piperidone precursor pL was synthesized according to a published procedure.²⁹

Caution! Metal perchlorates in presence of organic ligands are potentially explosive and sensitive to heat and impact. No problem occurred for the work described here but these compounds need in general to be handled with extreme care.

Electrochemistry was performed on a CH Instruments CHI660D electrochemical workstation, equipped with a CH



Fig. 5 (a) Temperature dependent susceptibility and (b) reduced magnetization of $[Mn^{II}(L)(Cl)]_2[MnCl_4]$.

Instruments Picoamp Booster. All electrochemical measurements were performed in a glass cell, covered with a teflon cap, situated in a Faraday cage. All complex solutions were prepared in degassed and with Argon saturated solvents. The supporting electrolyte for acetonitrile was: 0.1 M tetra-nbutylammonium tetrafluoroborate; for acetonitrile (MeCN): 0.1 M tetra-n-butylammonium hexafluorophosphate. Cyclovoltammograms (CVs) in non-aqueous media were recorded with an Ag/AgNO3 reference electrode, a glassy carbon working electrode and a platinum wire as counter electrode. Aqueous solutions contained 3 M sodium chloride (NaCl) as supporting electrolyte and were measured with an Ag/AgCl reference electrode, a glassy carbon working electrode and a platinum wire as counter electrode. Electrochemical measurements in nonaqueous media were normalized vs. ferrocene, where ferrocene had the following potential: MeCN (50 mV); in H₂O, potentials were normalized against potassium hexacyano ferrate $(K_3[Fe(CN)_6])$ with 270 mV.

UV/vis spectra were recorded with a Jasco V-570 UV-vis-NIR spectrometer as methanolic solutions.

NMR spectra were recorded with a Bruker Avance I (200 MHz) instrument; chemical shifts of 1 H and 13 C were referenced to solvent resonances (CDCl₃).

ESI-MS spectra were recorded on a Bruker ApexQe hybrid 9.4 T FT-ICR instrument.

Elemental analyses were obtained from a CHN-O-vario EL instrument by the "Mikroanalytisches Labor" of the chemical institutes, University of Heidelberg.

EPR measurements were performed on a Bruker ELEX-SYS-E-500 instrument and collected at liquid helium temperature in frozen methanol–ethanol (9:1) solution. The spin Hamiltonian parameters were obtained by simulation of the experimental data with the XSophe software package.^{48,49}

X-ray crystal structure determinations

Crystal data and details of the structure determinations are listed in the ESI (Table S3[†]). Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-Ka radiation, sealed tube, graphite monochromator; compounds [Fe^{II}(L)OHMe]²⁺ and [Fe^{III}(L)-OMe²⁺) or a Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-Ka radiation, microfocus tube, multilayer mirror optics; compounds $[Cu^{II}(L)]^{2+}$, $[Cu^{II}(L^{OH})]^{2+}$ and [Fe^{II}(L^{OH})Cl]⁺) or STOE IPDS I diffractometer (Mo-Ka radiation, graphite monochromator; compound $[Mn^{II}(L)Cl]^+$). Data were corrected for air and detector absorption, Lorentz and polarization effects;^{50,51} absorption by the crystal was treated numerically (Gaussian grid)⁵¹ (compounds [Cu^{II}(L)]²⁺ and $[Cu^{II}(L^{OH})]^{2+}$) or with a semiempirical multiscan method^{3,52,53} (all others). The structures were solved by conventional direct methods^{54,55} (compound [Mn^{II}(L)Cl]⁺) or by the charge flip procedure^{56,57} (all others) and refined by full-matrix least squares methods based on F^2 against all unique reflections.^{55,58} All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. Where possible, hydrogen atoms of solvent water were taken from difference Fourier syntheses or else placed to maximize hydrogen bonding^{59,60} with atomic charges calculated from partial equalization of orbital electronegativity.61 Water molecules were then refined as rigid groups. When found necessary, disordered groups and/or solvent molecules where subjected to suitable geometry and adp restraints.

In the structure of $[Fe^{II}(L^{OH})Cl]^+$ a cluster of 3 strong difference Fourier peaks was assigned to partially occupied sites of the chloride ion. Their total population refined to close to 1.0. The smtbx solvent masking procedure was then used to remove the electronic contribution of residual solvent molecules (water and/or methanol) from the Fobs.^{62,63} During refinement against the solvent-corrected data the sum of populations for the chlorides was restrained to 1.00(1). Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization (methanol and/or water) was removed from the structure of $[Mn^{II}(L)Cl]^+$ with the procedure,⁶² BYPASS as implemented in PLATON (SQUEEZE).^{64,65} Partial structure factors from the solvent masks were included in the refinement as separate contributions to F_{obs} .

Syntheses

Di(2-pyridyl)oxime.^{66,67} (C₁₁H₉N₃O, MW: 199.21 g mol⁻¹): To sodium acetate (2.96 g, 21.71 mmol, 2 eq.) in water (20.00 ml) was added hydroxylamine hydrochloride (1.51 g, 21.71 mmol, 2 eq.) and heated to 60 °C for one hour. Di(2pyridyl)ketone (2.0 g, 10.86 mmol, 1 eq.) was added in methanol (4.0 ml) and the brown solution was stirred at 60 °C overnight. The light red reaction mixture was cooled at 0 °C and the product precipitated in light-rose crystals. The product (2.10 g, 97% yield) was filtered, washed with a little cold water and dried *in vacuo*. FAB-MS: m/z = 200.10 (calc.: 200.08) [M + H]⁺; elemental analysis (report no.: 28891, C₁₁H₁₁N₃O₂) calc.: C(60.82), H(5.10), N(19.34), obs.: C(61.10), H(5.04), N(19.28).

Di(2-pyridyl)methylamine. ($C_{11}H_{11}N_3$, MW: 185.23 g mol⁻¹) The di(2-pyridyl)oxime (2.08 g, 10.44 mmol, 1 eq.), ammonium acetate (1.37 g, 17.75 mmol, 1.7 eq.) and concentrated ammonia (3.3 ml) were dissolved in ethanol-water (2:1, 63.0 ml) and heated to 80 °C. Zinc dust (3.07 g, 47.0 mmol, 4.5 eq.) was added in small portions during 30 minutes and the mixture was refluxed for additional 3 hours. After stirring at room temperature overnight, solids were removed by filtration, washed with a little water, and ethanol was removed at the rotary evaporator. The remaining solution was alkalized with 10 M sodium hydroxide solution and the amine was extracted with methylene chloride. The combined extracts were washed with brine, dried over sodium sulfate and evaporated. The crude product (1.37 g, 71% yield), a yellow-brown oil was used without further purification. ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 2.50 (br s, NH₂, 2H), 5.34 (m, CH, 1H), 7.14–7.17 (m, Harom., 2H), 7.39-7.41 (m, Harom., 2H), 7.62-7.66 (m, Harom., 2H), 8.57-8.58 (m, H_{arom.}, 2H), ¹³C-NMR (100 MHz, CDCl₃): *δ*[ppm] = 62.29, 121.73, 122.05, 136.66, 149.14, 162.69.

Di(2-pyridyl)methanol.^{66,67} (C₁₁H₁₀N₂O, MW: 186.21 g mol^{-1}): Sodium borohydride (1.03 g, 27.10 mmol, 1 eq.) was added in small portions to a solution of di(2-pyridyl)ketone (5.00 g, 27.10 mmol, 1 eq.) in methanol (50.0 ml) at 0 °C. The solution was warmed and stirred at room temperature overnight. The solvent was evaporated to dryness and the residue was taken up in water (20.0 ml) and acidified with 2 N hydrochloride acid. After stirring for 10 minutes, the solution was alkalized with concentrated ammonia and extracted with methylene chloride $(3 \times 50.0 \text{ ml})$. The combined organic extracts were dried with sodium sulfate and evaporated. The product (4.93 g, 98% yield), a brown oil was dried in vacuuo and used without further purification. ¹H-NMR (200 MHz, $CDCl_3$) δ [ppm] = 6.01 (s, CH, 1H), 6.05 (s, OH, 1H), 7.22-7.30 (m, $H_{\rm arom.},~2H),~7.60\text{--}7.64$ (m, $H_{\rm arom.},~2H),~7.70\text{--}7.77$ (m, $H_{\rm arom.},~2H),~8.58\text{--}8.61$ (m, $H_{\rm arom.},~2H),~^{13}\text{C-NMR}$ (50 MHz, CDCl₃): *δ*[ppm] = 74.66, 121.65, 122.80, 125.10, 126.23, 136.62, 137.55, 147.56, 149.13, 154.53, 160.42.

Di(2-pyridyl)methyl chloride.^{66,67} ($C_{11}H_9ClN_2$, MW: 204.6 g mol⁻¹): To a solution of di(2-pyridyl)methanol (4.61 g, 24.76 mmol, 1 eq.) in acetonitrile (52.0 ml) was added a solution of triphenylphosphine (7.79 g, 29.71 mmol, 1.2 eq.) in carbon tetrachloride (42.0 ml) at 0 °C over a period of

90 minutes drop wise. The solution was stored at +4 °C overnight and quenched with methanol (6.0 ml) for 15 minutes at room temperature. The initial volume was concentrated to 25.0 ml, dissolved in water (52.0 ml) and washed with chloroform $(2 \times 52.0 \text{ ml})$. The aqueous phase was neutralized with potassium carbonate and extracted with diethyl ether (4 \times 35.0 ml). The combined ether extracts were dried with sodium sulfate and evaporated. The crude product was obtained as a brown oil and purified by column chromatography (silica, $30 \times$ 6 cm, methylene chloride-methanol $10:1, R_f 0.46$). The analytically pure product was obtained as light-rose crystals (2.37 g, 47% yield). ¹H-NMR (200 MHz, CDCl₃) δ [ppm] = 6.24 (s, CHCl, 1H); 7.14-7.21 (m, 2H); 7.61-7.74 (m, 4H); 8.48-8.51 (m, 2H); 13 C-NMR (50 MHz, CDCl₃): δ [ppm] = 63.76 (, 123.10, 137.36, 148.79, 158.29, elemental analysis (C11H9ClN2): calc.: C (64.56), H(4.43), N(13.69), obs.: C(64.48), H(4.56), N(13.54).

Dimethyl-(7-benzyl-3-methyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate. (C29H30N4O5, MW: 514.57 g mol⁻¹): Benzylamine (3.44 ml, 31.55 mmol, 1.2 eq.) and formaldehyde (37% wt in water, 4.7 ml, 63.09 mmol, 2.4 eq.) were added to a suspension of the piperidone pL (10.0 g, 26.29 mmol, 1 eq.) in ethanol (60.0 ml) and refluxed for 4 hours. The black solution was stirred overnight at room temperature and the precipitated product was filtered and washed with ethanol. After recrystallization from ethanol, the product was obtained as a white powder (6.69 g, 49% yield). ¹H-NMR (200 MHz, CDCl₃) δ [ppm] = 2.01 (s, CH₃, 3H), 2.56–2.62 (d, ${}^{2}J_{H-H}$ = 11.87 Hz, CH_{2,eq}, 2H), 3.06–3.13 (d, ${}^{2}J_{H-H}$ = 12.09 Hz, CH_{2,ax}, 2H), 3.40 (s, NCH₂Ph, 2H), 3.86 (s, OCH₃, 6H), 4.73 (s, CH, 2H), 7.13-7.20 (m, H_{arom.}, 2H), 7.43-7.55 (m, $H_{\text{arom.}}$, 7H), 7.90–7.94 (d, ${}^{3}J_{\text{H-H}}$ = 7.80 Hz, $H_{\text{arom.}}$, 2H), 8.46–8.49 (m, $\mathbf{H}_{\text{arom.}}$, 2H), ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 43.26, 52.46, 59.01, 61.17, 62.47, 73.81, 122.87, 123.45, 127.65, 128.43, 130.42, 136.16, 136.94, 149.08, 158.47, 168.53, 203.65. ESI-MS, elemental analysis (C₂₉H₃₀N₄O₅, report no.: 31987): calc. C(67.88), H(5.88), N(10.89), obs.: C(67.83), H(5.90), N (10.82).

Dimethyl-(3-methyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo-[3.3.1]nonane)-1,5-dicarboxylate. (C₂₂H₂₄N₄O₅, MW: 424.45 g mol^{-1}) To a solution of 5 (4.0 g, 7.77 mmol, 1 eq.) in ethyl acetate (100.0 ml) was added palladium on activated charcoal (10%, 0.40 g) and the mixture was hydrated at 70 °C and 1 atm hydrogen overnight. The solvent was evaporated, the residue taken up in methylene chloride and the catalyst was removed by filtration over celite pad. After evaporation of the solvent, the crude product was recrystallized from ethanol as colorless needles (2.53 g, 77% yield). ¹H-NMR (200 MHz, CDCl₃) δ[ppm] = 1.73 (s, NCH₃, 3H); 3.07–3.21 (m, CH_{2 ax/eq}, 2H); 3.64 (s, OCH₃, 6H); 3.82–3.89 (m, CH_{2 ax/eq}, 2H); 4.56 (s, CH, 2H); 7.18–7.20 (m, H_{py} , 2H); 7.33–7.37 (m, H_{py} , 2H); 7.59–7.67 (m, H_{py}, 2H); 8.60–8.62 (m, H_{py}, 2H) ppm. ¹³C-NMR (50 MHz, $CDCl_3$) δ [ppm] = 41.61, 52.20, 55.06, 64.42, 73.73, 123.22, 124.39, 136.53, 150.05, 157.29, 168.70, 202.91. ESI-MS: m/z = 425.1 (100%), 426.1 (24%) [M + H]⁺, elemental analysis (C22H24N4O5, report no.: 31986): calc.: C(62.25), H(5.70), N(13.20), obs.: C(62.39), H(5.75), N(13.20).

Dimethyl-(3-methyl-7-bis(2-pyridyl)methyl-9-oxo-2,4-bis-(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate (L). $(C_{33}H_{32}N_6O_5, MW: 592.64 \text{ g mol}^{-1})$: Method A: to a suspension of the piperidone pL (2.74 g, 2.7 mmol, 1 eq.) in methanol (15.0 ml) was added di(2-pyridyl)methylamine (1.60 g, 8.64 mmol, 1.2 eq.) and formaldehyde (37% wt in water, 1.3 ml, 17.28 mmol, 2.4 eq.) and was refluxed for 1 hour. After evaporation of the solvent, the residue was recrystallized from hot ethanol to obtain the product as a white powder (0.67 g)16% yield). Method B: di(2-pyridyl)methyl chloride (0.50 g, 2.44 mmol, 1 eq.) was refluxed for 24 hours with 6 (1.03 g, 2.44 mmol, 1 eq.), sodium carbonate (0.52 g, 4.89 mmol, 2 eq.) and a catalytic amount of sodium iodide in acetonitrile (10.0 ml). After complete evaporation of the solvent, the residue was partitioned between water and methylene chloride, the organic phase was separated, the aqueous phase was extracted with methylene chloride and the combined organic extracts were dried over sodium sulfate. After evaporation of the solvent the residue was recrystallized from ethanol to obtain the product as a white powder (0.76 g, 53% yield). ¹H-NMR (200 MHz, CDCl₃) δ [ppm] = 1.89 (s, NCH₃, 3H), 3.03–3.09 (d, ${}^{2}J_{H-H}$ = 12.3 Hz, CH_{2,ax}, 2H), 3.46–3.52 (d, ${}^{2}J_{H-H}$ = 11.4 Hz, CH_{2.eq}, 2H), 3.67 (s, OCH₃, 6H), 4.47 (s, CH, 2H), 4.75 (s, NCH, 1H), 7.03-7.10 (m, H_{py}, 4H), 7.49-7.66 (m, H_{py}, 6H), 7.76–7.80 (d, ${}^{3}J_{H-H}$ = 7.8 Hz, H_{py}, 2H), 8.36–8.49 (m, H_{py}, 4H), ¹³C-NMR (50 MHz, CDCl₃) δ [ppm] = 42.45, 52.36, 56.31, 63.08, 74.34, 77.95, 122.46, 122.84, 124.20, 124.48, 136.26, 149.08, 149.18, 157.90, 159.23, 168.82, 202.73, elemental analysis (C₃₃H₃₂N₆O₅, report no.: 32196): calc.: C(66.88), H(5.44), N(14.18), obs.: C(66.67), H(5.56), N(14.08).

Dimethyl-(3-methyl-7-bis(2-pyridyl)methyl-9-hydroxo-2,4-bis-(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate (L^{OH}). (C₃₃H₃₄N₆O₅, MW: 594.66 g mol⁻¹): The ligand L (0.32 g, 0.54 mmol, 1 eq.) was dissolved in 1,4-dioxane-water-mixture 3:1 (12.0 ml) an cooled to -5 °C, sodium borohydride (0.01 g, 0.27 mmol, 0.5 eq.) in 1,4-dioxane-water-mixture 2:1 (4.0 ml) was added drop wise. The solution was allowed to warm up to 0 °C and was stirred overnight. The solution was acidified with concentrated sulfuric acid until the solution remained clear. After stirring for 3 hours at 0 °C, the solution was alkalized with sodium hydroxide solution (20 wt% in water) and L^{OH} was extracted with methylene chloride. After drying the organic extracts over sodium sulfate and evaporating the solvent, and recrystallizing from ethanol, the product was obtained as a white powder (0.30 g, 93% yield). ESI-MS (pos): $m/z = 595.2 [L^{OH} + H]^+$, 617.3 $[L^{OH} + Na]^+$, elemental analysis (C35H40N6O6, report no.: 29984) calc. C(66.11), H(6.03), N(13.61), obs. C(66.01), H(5.77), N(13.83).

[Cu^{II}(L)](BF₄)₂·3H₂O. Solutions of L (100 mg, 168.73 µmol, 1 eq.) in MeCN (4.0 ml) and dry Cu(BF₄)₂ (40 mg, 168.73 µmol, 1 eq.) in MeCN (1.0 ml) were combined and the deep blue solution was refluxed for 1 hour. The solvent was evaporated to dryness and the residue was taken up in MeOH and subjected to diethyl ether diffusion to obtain blue needles (104 mg, 74% yield). UV/vis $\lambda = 626$ nm (15 974 cm⁻¹), $\varepsilon = 119$ M⁻¹ cm⁻¹; CV: -651 mV (MeCN vs. Fc/Fc⁺), -786 mV (H₂O vs.

K₃[Fe(CN)₆]), Elemental analysis (report no.: 32312): calc. (%): C(44.84), H(4.33), N(9.51); obs. (%): C(44.66), H(4.35), N(9.38).

[Cu^{II}(L^{OH})](BF₄)₂·2H₂O. (C₃₃H₃₄B₂CuF₈N₆O₅, MW: 831.82 g mol⁻¹): L^{OH} (0.05 g, 0.08 mmol, 1 eq.) was dissolved in hot acetonitrile (4.0 ml), after addition anhydrous Cu(BF)₄ (0.02 g, 0.08 mmol, 1 eq.) in acetonitrile (1.0 ml), the deep blue solution was heated to reflux once and stirring was continued at room temperature overnight. The blue solution was subjected to diethyl ether diffusion to obtain blue needles (39 mg, 54% yield) suitable for X-ray diffraction. UV/vis λ = 630 nm (15 873 cm⁻¹), ε = 112 M⁻¹ cm⁻¹; CV: -671 mV (MeCN *vs.* Fc/Fc⁺), -728 mV (H₂O *vs.* K₃[Fe(CN)₆]). Elemental analysis (report no. 32312) calc. (%): C(45.67), H(4.41), N(9.68); obs. (%) C(45.67), H(4.52), N(9.72).

[Cu^{II}(L)](ClO₄)₂·MeOH. A suspension of L (0.15 g, 253.10 μmol, 1 eq.) in MeOH (1.5 ml) was combined with a solution of Cu(ClO₄)₂·6H₂O in MeOH-H₂O (1 : 1, 3.0 ml) and the resulting blue solution was refluxed for 60 minutes. After the solution was concentrated to one half of the initial volume and stored at +4 °C the product crystallized as blue plates (180 mg, 80% yield). CV: -678 mV (MeCN *vs.* Fc/Fc⁺). Elemental analysis (report no. 32341) calc. (%): C(46.03), H(4.09), N(9.47); obs. (%) C(45.85), H(4.26), N(9.63).

 $[Fe(L^{OH})Cl](Cl)$. (C₃₃H₃₄Cl₂F_eN₆O₅, MW: 721.41 g mol⁻¹): L^{OH} (25 mg, 0.04 mmol, 1 eq.) was suspended in dry acetonitrile (2.0 ml), anhydrous FeCl2 was added under argon atmosphere, and the yellow solution was stirred at room temperature overnight. The yellow solution was subjected to diethyl ether diffusion to obtain yellow needles (15.9 mg, 52%), diffraction. suitable for X-ray Elemental analysis (C₆₆H₇₄Cl₄Fe₂N₁₂O₁₃, report no. 32313) calc. C(52.96), H(4.98), N(11.23), obs. C(53.03), H(4.91), N(11.11), UV/vis (MeCN): $\lambda =$ 412 nm (24 271 cm⁻¹), ε = 1381 M⁻¹ cm⁻¹, 341 nm (29 326 cm⁻¹), ε = 1712 M⁻¹ cm⁻¹, 259 nm (38 610 cm⁻¹), ε = 10 996 M⁻¹ cm⁻¹; CV: 225 mV (MeCN vs. Fc/Fc⁺), FAB-MS (NPOE-Matrix) $m/z = 683.22 \, [Fe(L^{OH})(Cl)]^+, 701.24 \, [Fe(L^{OH})-$ (Cl)]⁺ + H₂O, 715.28 [Fe(L^{OH})(Cl)]⁺ + MeOH.

[Fe(L)(OMe)](ClO₄)₂: L (50.0 mg, 0.08 mmol, 1 eq.) was suspended in methanol (4.0 ml), Fe(ClO₄)₂ (41 mg, 0.17 mmol, 2 eq.) was added and the yellow complex precipitated. The mixture was stirred at room temperature over-night, the solid was filtered of and dried under vacuum. The raw product was taken up in acetonitrile and subjected to diethylether diffusion to obtain yellow-brown needles (36 mg, 49%), suitable for X-ray diffraction. Evans-NMR: $\mu_{\text{eff}} = 5.1882$ B.M., molar susceptibility 1.1415 × 10⁻² cm³ mol⁻¹.

[Fe(L)(HOMe)](BF₄)₂: under argon atmosphere L (100 mg, 0.17 mmol, 1 eq.) was stirred with Fe(BF₄)₂·6H₂O (57 mg, 0.17 mmol, 1 eq.) in methanol (3.0 ml) at room temperature over-night. The yellow solution was subjected to diethylether diffusion to obtain yellow needles (78 mg, 54%) suitable for X-ray diffraction. Elemental analysis calc. C(46.67), H(4.41), N(9.68), obs. C(45.76), H(4.52), N(9.72), UV/vis (MeCN): λ = 364 nm (27 472 cm⁻¹), ε = 1245 M⁻¹ cm⁻¹, CV: 474 mV (H₂O vs. K₃[Fe(CN)₆]), Evans-NMR: μ_{eff} = 4.9613 B.M., molar susceptibility 1.0438 × 10⁻² cm³ mol⁻¹.

 $[MnCl(L)]_2[MnCl_4]$. L (50.0 mg, 0.08 mmol, 1 eq.) was suspended in acetonitrile (2.0 ml) and heated to 50 °C until complete solution of the ligand. $MnCl_2 \cdot 4H_2O$ (17.0 mg, 0.08 mmol, 1 eq.) in acetonitrile-methanol 1 : 1 (2.0 ml) was added, and the colorless solution was stirred at room temperature overnight. The solvent was evaporated the residue was redissolved in methanol. The supernatant was separated and subjected to diethyl ether diffusion, to obtain colorless needles (33 mg, 56%), suitable for X-ray diffraction. Elemental analysis calc. C(48.18), H(4.97), N(9.63), obs. C(48.13), H(4.55), N(9.63), magnetic susceptibility: 4.168 cm³ K mol⁻¹, CV: (MeCN) 791 mV (ν s. Fc/Fc⁺).

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