Universiteit
Leiden
The Netherlands

Copper complexes as biomimetic models of catechol oxidase: mechanistic studies

Koval, I.A.

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2 Synthetic route to novel asymmetric dinucleating ligands. Crystal structure and properties of the complex $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ †

In this chapter the synthesis of the new asymmetric ligand 2-[*N,N*-bis(2-pyridylmethyl)aminomethyl]-4-methyl-6-[(2-pyridylmethyl)aminomethyl]phenol (Hpy3asym), which was conceived to model the asymmetry in the active site of catechol oxidase, is reported. This phenol-based "end-off" compartmental ligand holds one tridentate and one didentate arm attached to the 2 and 6 positions of the phenolic ring. A dinuclear copper(II) nitrate complex with this ligand $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ has been obtained and structurally characterized. In this complex both copper ions have a distorted octahedral geometry and are endogenously bridged by the phenolic oxygen atom of the deprotonated ligand. The complex shows a donor-atom asymmetry that consists of a N_3O_3 donor set for the Cu1 ion and a N_2O_4 donor set for the Cu2 ion. The spectral properties of the complex, as well as its electrochemical and magnetic behavior, are discussed.

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2.1 Introduction

The term "dinucleating ligands" was first introduced in 1970 by Robson[1] to describe a class of polydentate chelating ligands, able to bind simultaneously two metal ions. Since then, a very large number of such ligands were designed, and their coordination compounds were thoroughly investigated. The possible applications of the complexes with this type of ligands vary from modeling the active sites of many metalloenzymes,[2-4] to hosting and carrying small molecules[5-7] or homogeneous catalysis.[8,9]

Among many different types of dinucleating ligands, the phenol-based compartmental ligands attracted particularly wide attention of scientists. The term "compartmental" was introduced to indicate a ligand containing two adjacent, but dissimilar coordination sites.[2] Particular interest in this type of ligands resulted from the recent recognition of the asymmetric nature of a number of dimetallic biosites.[10,11] The understanding of the ability of individual metal ions to play possibly different functions in dinuclear sites in metalloenzymes led to the design of a large number of asymmetric ligands where two compartments would provide a different coordination surrounding for the two metal ions.

As stated in Chapter 1, the active site of catechol oxidase is asymmetric, which led to the proposal that during the catalytic cycle, the binding of the substrate occurs to only one of the metal centers (CuB). Taking the inspiration from the natural molecule, the attention has been turned to the deliberate design of novel model systems of the type-3 active site, where the two copper ions would have distinctly different coordination surroundings. The site specificity of the copper ions may help to answer an important question concerning the binding of the substrate in the natural enzyme, *e.g.* is the catechol substrate forming a bridge between the two copper(II) centers rather than binding to only one of them?

In this chapter, the synthesis of the novel phenol-based ligand 2-[*N,N*-bis(2-pyridylmethyl)aminomethyl]-4-methyl-6-[(2-pyridylmethyl)aminomethyl]phenol, Hpy3asym, is described. In this ligand, the 2 and the 6 positions of the phenol-ring are substituted by a tridentate and a didentate arm containing nitrogen donor atoms, providing two copper ions with different coordination surroundings. The crystal structure, spectroscopy, electrochemical and magnetic behavior of a new asymmetric dicopper(II) complex with this ligand are reported.

2.2 Results and Discussion

2.2.1 Synthesis

The ligand Hpy3asym has been synthesized in four steps (Figure 2.1) from commercially available 5-methylsalicylaldehyde. The first step includes the introduction of a methylene chloride group in the 3' position of the phenol ring. The chloride atom is

subsequently substituted by di-(2-picolyl)amine. Finally, the reductive amination of the aldehyde group by 2-aminomethylpyridine and sodium borohydride leads to the desired ligand.

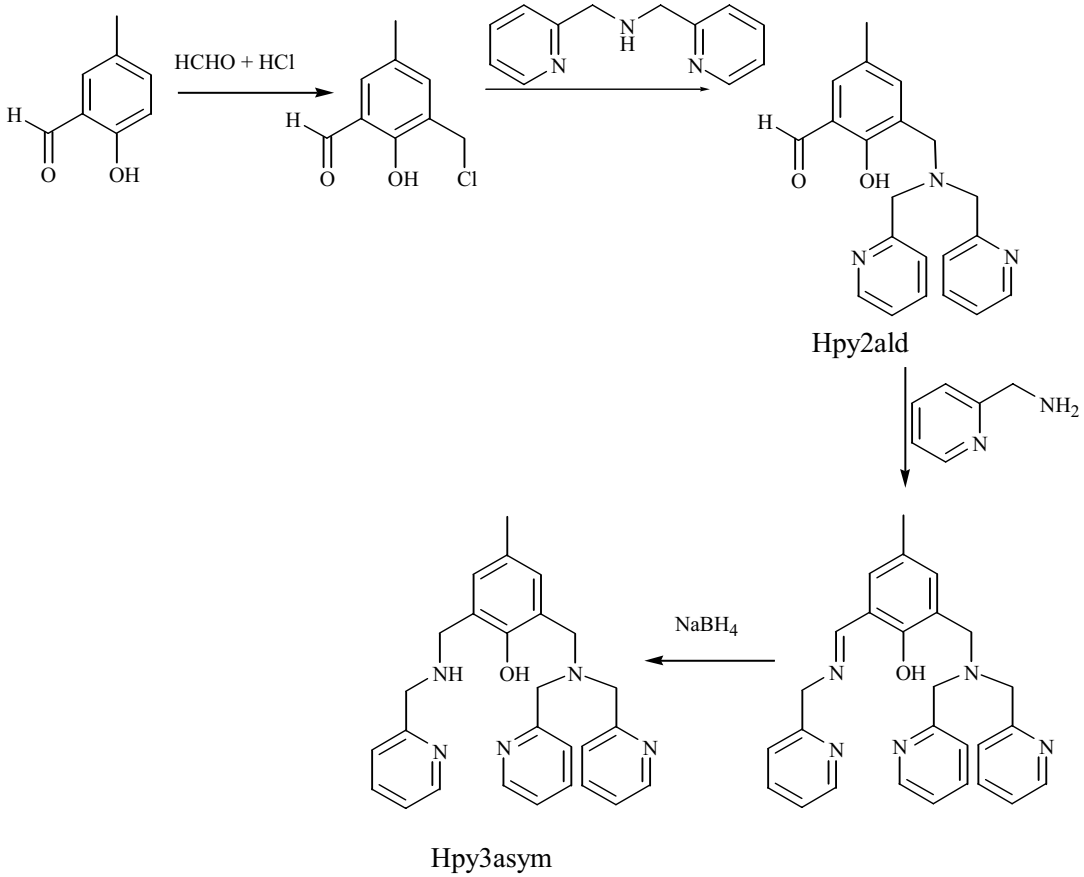

Figure 2.1. The reaction scheme of the synthesis of the phenol-based compartmental "end-off" ligand Hpy3asym

The straightforward synthetic pathway, developed for the synthesis of Hpy3asym, can also be successfully applied for the preparation of other dinucleating asymmetric ligands, with variations in the number and type of the donor atoms, as reported elsewhere.[12]

The dicopper(II) complex $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ (**1**) has been prepared by mixing one molar equivalent of the ligand with two equivalents of copper(II) nitrate in an acetonitrile/water mixture. The evaporation of the solvent and washing of the residue with small amounts of acetone resulted in the pure compound.

2.2.2 Crystal structure description

Very small green rectangular crystals of **1** have been obtained by slow evaporation of an acetonitrile solution of the complex. An ORTEP projection of the complex is depicted in Figure 2.2 (left), selected bond lengths and bond angles are given in Table 2.1. The compound crystallizes in the space group $P2_1/n$. Both copper ions have specifically different coordination surroundings, showing a donor-atom

asymmetry. An endogenous phenolato bridge is present in the dinuclear core, but no exogenous bridge is present. The N_3O_3 coordination sphere around the Cu1 ion can be regarded as a very distorted octahedron. The equatorial plane is formed by the tertiary amine nitrogen atom N1 at a distance of 2.0182(18) Å, two *trans* located nitrogen atoms N2 and N3 from two pyridine rings at a distance of 1.9860(17) Å and 1.9760(18) Å, respectively, and the oxygen atom O2 from a water molecule at a distance of 1.9701(16) Å. One of the axial positions is occupied by the bridging phenolate oxygen atom O1 at a relatively long distance of 2.3070(13) Å. The second apical position has a weak O-donor ligand, which was refined for 50% to be water and for 50% a disordered nitrate anion. The oxygen atom O20 (occupancy 0.4886) from the water molecule is at a distance of 2.535(3) Å. The loosely bound oxygen atom O10 (occupancy 0.5114) from the disordered nitrate counter anion (the Cu1-O10a distance is 3.007(6) Å) is at a much larger distance, which, however, still matches the range of bond lengths observed for copper-oxygen bonds along the Jahn-Teller axis.[13-16] The in-plane *cis* angles around the Cu1 ion vary in quite a broad range, *viz.* 83.92(8)º for the N1-Cu1-N3 angle and 96.92(7)º for the O2-Cu1-N2 angle. Their sum amounts to 357.76º. The O-Cu1-O angle along the Jahn-Teller axis is equal to 173.85(8)º for the O1-Cu1-O20 angle and 165.46(10)º for the O1-Cu1-O10 angle, thus indicating a significant distortion from the regular octahedral geometry.

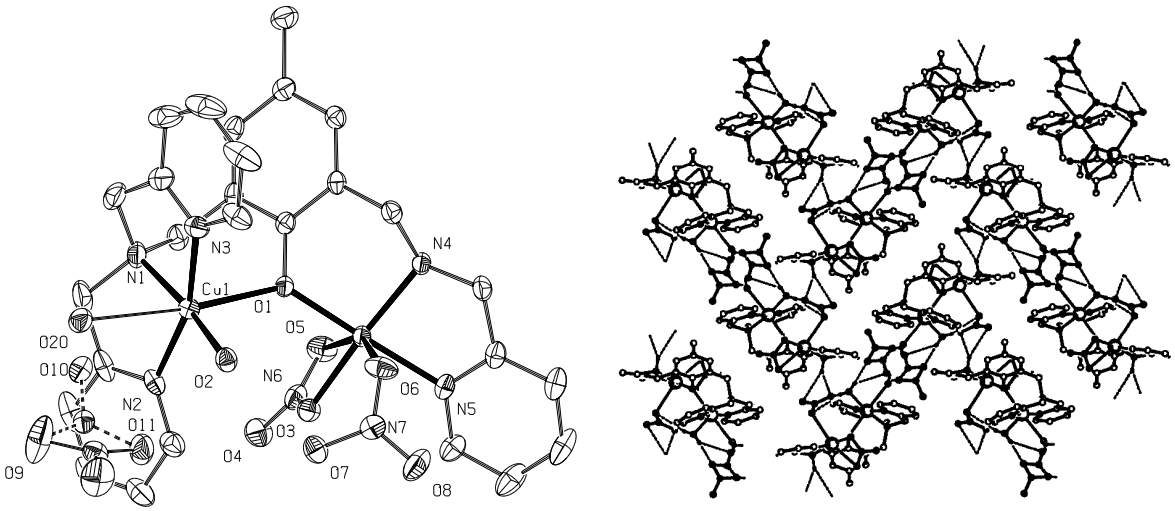

Figure 2.2. Left: ORTEP projection of $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ (**1**). The hydrogen atoms are omitted for clarity. The second axial position at Cu1 ion has a O-donor ligand, which was found in 50% to be water and in 50% a disordered nitrate anion (see text for further details). Right: PLATON[17] projection of a "herring-bone" packing arrangement along the crystallographic *a* axis. All hydrogen atoms, besides those participating in hydrogen bonding, are omitted.

The absence of an exogenous bridge between the two copper ions promotes the large copper-copper separation of 3.9003 Å, which is significantly longer than the distances observed for the similar complexes with two types of bridges between the copper ions.[5,9,18,19] It is interesting to notice that potentially bridging nitrate anions are

present in the complex; however, they fail to bridge the two copper ions, instead being coordinated as monodentate and didentate chelating ligands. The distribution of charged and neutral ligands in the complex is also remarkable: one neutral water molecule is coordinated to the Cu1 ion, whereas two charged nitrate anions are coordinated to the Cu2 ion.

Table 2.1. Selected bond distances and bond angles for **1**

Bond lengths (Å)			
Cu1 – O2	1.9700(16)	Cu2 – N4	1.9841(17)
Cu1 – N3	1.9767(19)	Cu2 – N3	1.9907(15)
Cu1 – N2	1.9866(18)	Cu2 – N5	2.0167(17)
Cu1 - O1	2.3069(14)	Cu2 – O5	2.5438(16)
Cu1 – O20	2.548(3)	Cu2 – O6	2.5985(17)
Cu1 – O10	3.010(3)	Cu2 – O1	1.9357(14)

Bond angles (°)			
Cu1 – O21 – Cu2	133.49(7)		
O2 – Cu1 – N2	96.92 (7)	O1 – Cu2 – N4	94.66(6)
N3 – Cu1 – N2	163.36(8)	O1 – Cu2 – O3	90.71(6)
O2 – Cu1 – N1	84.46(8)	N4 – Cu2 – O3	170.49(7)
N2 – Cu1 – N1	83.88(8)	O1 – Cu2 – N5	172.59(7)
O2 – Cu1 – O1	96.90(6)	N4 – Cu2 – N5	82.45(7)
N3 – Cu1 – O1	90.21(6)	O3 – Cu2 – O5	93.13(7)
N2 – Cu1 – O1	102.18(6)	O1 – Cu2 – O5	87.36(6)
N1 – Cu1 – O1	92.85(6)	N4 – Cu2 – O5	116.56(7)
O2 – Cu1 – O20	87.70(9)	O1 – Cu2 – O6	95.52(6)
N2 – Cu1 – O20	81.22(9)	N4 – Cu2 – O6	85.63(6)
O1 – Cu1 – O20	173.85(8)	O3 – Cu2 – O6	101.68(5)
O2 – Cu1 – O10	71.82(8)	N5 – Cu2 – O6	77.49(6)
N3 – Cu1 – O10	98.72(8)	O5 – Cu2 – O6	157.38(5)
N1 – Cu1 – O20	82.36(9)		
N3 – Cu1 – O20	85.50(9)		
N3 – Cu1 – O10	98.72(8)		
N2 – Cu1 – O10	71.50(8)		
N1 – Cu1 – O10	98.97(8)		
O1 – Cu1 – O10	165.78(7)		
O20 – Cu1 – O10	20.35(8)		

The coordination sphere around the second copper ion Cu2 can also be described as a distorted octahedron, but with a N_2O_4 donor set. The equatorial plane around the Cu2 ion is formed by two *cis* located nitrogen atoms N4 from the secondary amine (the Cu2-N4 distance is 1.9838(17) Å) and N5 from the pyridine ring (the Cu2-N5 distance is 2.0181(17) Å), and two *cis* oxygen atoms, O1 from the bridging phenolate (the Cu2-O1 distance is 1.9353(14) Å) and O3 from the chelating nitrate

anion (the Cu2-O3 distance is 1.9910(14) Å). The second oxygen atom O5 from the chelating nitrate anion and the oxygen atom O6 from the monocoordinated nitrate anion occupy the axial positions, thus adjusting the coordination sphere around the copper ion to a very distorted octahedron (the distances Cu2-O5 and Cu2-O6 are equal to 2.5431(16) Å and 2.5982(16) Å, respectively). The in-plane *cis* angles vary in the range 87.36º-94.64º. The angle O5-Cu2-O6, which should be equal to 180º in the regular octahedron, is only 157.37(5)º, indicating an even greater distortion from the regular octahedron geometry than observed in the case of the Cu1 ion.

The crystal packing is stabilized by an extensive net of intra- and intermolecular hydrogen bonds (see Table 2.2). In particular, a bifurcated intramolecular hydrogen bonding is realized between the proton H2b of the water molecule coordinated to the Cu1 ion and the two oxygen atoms O6 and O7 of the monodentate nitrate anion coordinated to the Cu2 ion, giving an impression of exogenous pseudo-bridge between the two copper ions. Furthermore, each formula unit is connected via intermolecular hydrogen bonds to three neighboring units. The PLATON[17] projection of the crystal packing along the crystallographic *a* axis is shown in Figure 2.2 (right). As can be seen, the molecules are assembled by means of hydrogen bonds to form a "herring-bone" pattern.

Table 2.2. Hydrogen bonds (D-H…A) with the distance H…A < r(A) + 2.000 Å and the angle DHA > 110°.

Donor - H....Acceptor	*D – H (Å)*	*H...A (Å)*	*D...A (Å)*	*D - H...A (º)*
O2 - H2a...O11	0.736	1.971	2.704	174.09
O2 - H2a...O10	0.736	2.518	3.026	127.91
O2 - H2b...O7	0.915	1.802	2.657	154.44
O2 - H2b...O6	0.915	2.448	3.245	145.50
N4 - H4...O7 [x-1/2,-y+1/2,z-1/2]	0.930	2.119	2.917	143.16
O20 - H20a...O9 [-x,-y,-z+1]	0.759	2.087	2.821	163.07
O20 - H20b...O9	0.999	2.010	2.985	164.96
O20 - H20b...O11	0.999	2.486	3.191	127.27

2.2.3 Physical characterization

Besides the crystal structure determination, the complex has been spectroscopically and magnetically characterized. Electrospray mass spectra (ESI-MS) of the complex performed in acetonitrile reveal one major peak at *m/z* 688, corresponding to $[Cu_2(py3asym)(NO_3)_2]^+$. The theoretical isotopic pattern calculated for the empirical formula $C_{27}H_{28}Cu_2N_7O_7$ is in agreement with the experimentally found one. Thus, the 1.5 water molecules coordinated to the Cu1 ion, observed in the solid state, are lost during the measurement. The UV-Vis spectrum of the solid exhibits two

peaks at 456 and 640 nm. The first peak is assigned to a LMCT transition between the bridging phenoxo group and copper ions,[9] whereas the second one is characteristic for Cu^{II} d-d transitions.[20] The positions of these bands do not significantly change when the spectrum of the complex is taken in acetonitrile solution, suggesting no important modifications in the copper-ligand chromophores.

A cyclic voltammogram of the complex recorded in acetonitrile, when scanning towards the negative region of potentials, shows two successive one-electron electrochemical signals. The first one at -0.13 V *vs.* Ag/AgCl is assigned to the $Cu^{II,II}{}_2/Cu^{II,I}{}_2$ redox-couple. The second one at -0.33 V is attributed to the formation of $Cu^{I,I}{}_2$ species. They both appear to be irreversible. In addition, a very broad peak at ca. -0.7 V suggests the reduction of both copper ions to Cu^0 and the deposit of the free metal on the electrode surface. On the reverse scan, an additional sharp anodic peak is observed at -0.27 V. This is the so-called stripping peak, caused by the redissolution of the metallic copper. This peak is absent if the potential sweep is reversed at ca. -0.5 V, before the reduction to Cu^0 could take place. The anodic part of the cyclic voltammogram is characterized by three successive fully irreversible oxidation waves at 1.16, 1.48 and 1.68 V, apparently corresponding to the oxidation of the ligand and/or water molecules.

2.2.4 Magnetic properties

In Figure 2.3, the magnetic susceptibility of **1** is shown, plotted as both χ^{-1} and χ versus the temperature. The compound displays a weak ferromagnetic coupling with a Curie temperature θ of 0.87 K and a Curie-Weiss constant C of 0.39 cm^3 K mol^{-1}. The value for μ is 1.10 B.M.

The magnetic properties of this dinuclear copper(II) complex have been interpreted in terms of the Bleaney-Bowers equation (2.1),[21] where g is the magnetic field splitting factor, J is the exchange integral of magnetic theory and TIP is a Temperature Independent Paramagnetism term of 1 mole of copper(II) ions.

$$\chi_M = \frac{2g^2N\beta^2}{kT\,[3 + exp\,(-J/kT)]} + TIP \qquad (2.1)$$

The fit was accomplished by minimization of the reliability factor, defined as $R = \Sigma(\chi_m T_{calc} - \chi_m T_{obs})^2/(\chi_m T_{obs})^2$, by a least-squares procedure. The best fit was obtained for the exchange integral J = -4.6 cm^{-1}, the magnetic field splitting factor g = 2.02 and $R = 2.9\times10^{-3}$.

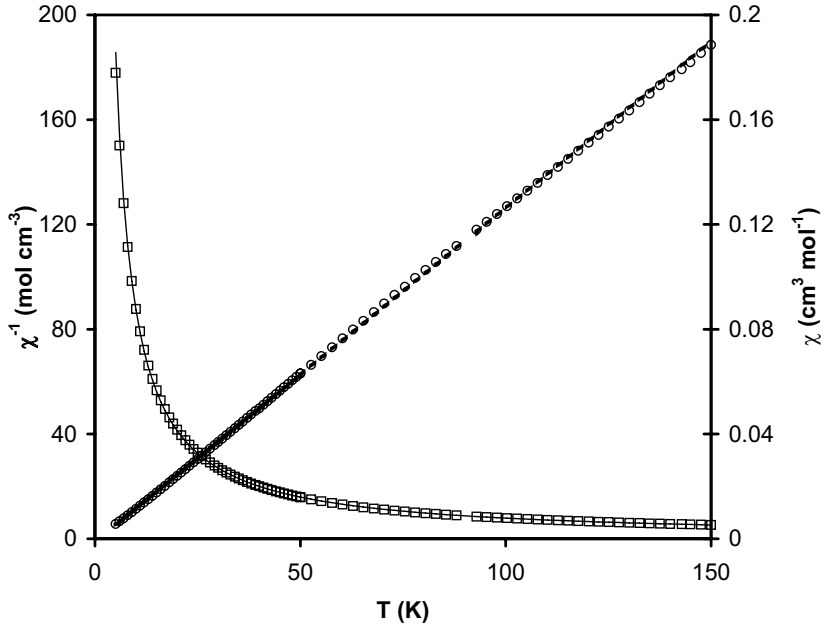

Figure 2.3. Magnetic susceptibility plotted as χ^{-1} versus *T;* (O) and as χ versus T; (□). The dashed line is the Curie-Weiss plot from near field theory, the solid line is the theoretical curve according to the Bleaney-Bowers equation.

2.2.5 Relevance to the active site of catechol oxidase

Similarly to the *met* state of natural enzyme, the dicopper(II) core in the complex comprises a single bridging oxygen atom, provided by the deprotonated phenolate moiety of the ligand. However, the two metal ions are being held on a long distance of 3.9003 Å, which is significantly larger than 2.9 Å, the Cu…Cu distance reported for the *met* form of catechol oxidase.[10] In addition, although the ligand has been designed to yield a coordination number asymmetry at the dimetal core, with its two pendant arms providing, respectively, three and two nitrogen donor atoms for coordination, it can be seen that each copper ion is coordinated by six donor atoms, with the coordination sphere being completed to a distorted octahedral surrounding by counter ions and solvent molecules. The complex shows thus a donor atom asymmetry instead, and its structure only vaguely resembles that of the natural enzyme, in which both copper ions have a distorted trigonal pyramidal coordination sphere with an N_3O donor set (see Chapter 1). However, the developed synthetic pathway for the synthesis of this ligand and other asymmetric dinucleating compartmental ligands opens new possibilities for the design of new model systems and allows easy variations in the number and the type of donor atoms surrounding each metal ion (Chapters 3-5). It should also be noted that the presence of other potentially bridging ligands, *e.g.* hydroxide anions, may lead to a significantly shorter metal-metal distances in the dicopper core, making the respective complexes promising functional models of catechol oxidase.

2.3 Experimental Section

2.3.1 Materials and Methods

Most of the synthetic work was carried out using standard Schlenk techniques. All chemicals were commercially available and used without further purification. 5-methylsalicylaldehyde was purchased from Fluka, 2-(aminomethyl)pyridine from Acros, and di-(2-picolyl)amine from Aldrich. 3-chloromethyl-5-methylsalicylaldehyde was prepared according to the procedure described by Lock.[22] Tetrahydrofuran and methanol were dried by reflux over sodium. C,H,N determinations were performed on a Perkin Elmer 2400 Series II analyzer. NMR spectra were recorded on a JEOL FX-200 (200MHz) FT-NMR spectrometer. Solid-state ligand field spectra (300-2000 nm, diffuse reflectance) and in solution were taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. IR spectra were recorded as pure solid on a Perkin Elmer FT-IR Paragon 1000 spectrophotometer with a Specac single-reflection diamond ATR P/N 10500, using the diffuse reflectance technique (4000-300 cm^{-1}, res. 4 cm^{-1}). Electrospray mass spectra (ESI-MS) were recorded on the Thermo Finnigan AQA apparatus. Cyclic voltammetry measurements were performed with an Autolab PGSTAT 10 cyclic voltammeter, using a Pt working electrode and a Ag/AgCl reference electrode in acetonitrile (10^{-3} M), with tetrabutylammonium perchlorate as supporting electrolyte, at a scan rate of 0.1 V/s. DC magnetic susceptibility measurements (5-150 K) were carried out at 0.1 Tesla using a Quantum Design MPMS-5 5T SQUID magnetometer. Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.3.2 Ligand synthesis

3-[*N,N*-bis(2-pyridylmethyl)aminomethyl]-5-methylsalicylaldehyde (Hpy2ald): A solution of di-(2-picolyl)amine (1.08 g, 5.4 mmol) and triethylamine (1.09 g, 10.8 mmol) in 50 ml of dry THF was added dropwise upon stirring to a solution of 3-chloromethyl-5-methylsalicylaldehyde (1 g, 5.4 mmol) in 250 ml of dry THF under Ar atmosphere. After completion of the addition, the resulting white suspension was refluxed for two hours and cooled to room temperature. After the removal of the triethylamine hydrochloride salt by filtration, the resulting solution was evaporated under reduced pressure, yielding a yellow oil, from which the product crystallized within a few minutes. The recrystallization from methanol-diethyl ester mixture gave slightly yellowish crystals of the pure compound. Yield: 1.55 g, 4.5 mmol (82%). ^{1}H-NMR ($CDCl_3$, 200 MHz, ppm): δ = 10.42 (s, 1H, aldehyde proton), 8.56 (d, 2H, 6'py-H); 7.63 (td, 2H, 4'py-H); 7.40 (td, 2H, 5'py-H); 7.21(s, 1H, 6'phenol-H); 7.18 (d, 2H, 3'py-H); 7.13 (s, 1H, 4'phenol-H); 3.89 (s, 4H, N-(CH_2py)$_2$); 3.80 (s, 2H, phenol-CH_2-N); 2.23 (s, 3H, CH_3) .

2-(bis(2-pyridylmethyl)aminomethyl)-4-methyl-6-[(2-pyridylmethyl)iminomethyl]phenol: A solution of 2-pyridylmethylamine (0.39 g, 3.6 mmol) in 50 ml of dry methanol was added dropwise upon stirring to a solution of Hpy2ald (1.26 g, 3.6 mmol) in 250 ml of dry methanol under argon. After the addition was complete, the resulting bright yellow solution was heated for two hours at 50 °C. The successful formation of the imine derivative was verified by NMR. ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ = 8.51 (d, 3H, 6'py-H); 8.34 (s, 1H, CH=N); 7.62 (td, 3H, 4'py-H); 7.33 (t, 3H, 5'py-H); 7.26(d, 2H, 3'py-H); 7.09 (s, 1H, 3'phenol-H); 7.03 (2, 1H, 5'phenol-H); 4.92 (s, 2H, CH=N-CH_2) 3.88 (s, 4H, N-(CH_2py), 3.80 (s, 2H, phenol-CH_2-N); 2.29 (s, 3H, CH_3).

2-[bis(2-pyridylmethyl)aminomethyl]-4-methyl-6-[(2-pyridylmethyl)aminomethyl]phenol (Hpy3asym): 0.41 g (10.9 mmol, 3 eq/1CH=N) of $NaBH_4$ were added *in situ* to a solution of 2-(bis(2-pyridylmethyl)aminomethyl-4-methyl-6-[(2-pyridylmethyl)iminomethyl]phenol in methanol. After the hydrogen evolution stopped, the resulting colorless solution was refluxed for two hours and evaporated under reduced pressure. The residue was dissolved in acidified water and washed three times with dichloromethane. The water layer was made alkaline (pH~9) by addition of concentrated ammonia. The resulting white suspension was extracted three times with dichloromethane. The organic layers were collected and dried over Na_2SO_4. After evaporation under reduced pressure, the pure compound was obtained as clear yellow oil. Yield: 1.54 g, 3.5 mmol (96%). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ = 8.55 (d, 3H, 6'py-H); 7.59 (td, 3H, 4'py-H); 7.36 (d, 3H, 3'py-H); 7.14 (t, 3H, 5'py-H); 6.93 (s, 1H, 3'phenol-H); 6.84 (s, 1H, 5'phenol-H); 3.95 (s, 2H, NH-CH_2-py); 3.91 (s, 2H, phenol-CH_2-NH); 3.85 (s, 4H, N-(CH_2-py)$_2$); 3.75 (s, 2H, phenol-N-CH_2); 2.22 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm): δ = 159.35; 154.80; 147.32; 136.17; 128.35; 126.35; 124.00; 123.11; 122.85; 121.67; 59.06; 56.12; 54.65; 50.95; 26.22.

2.3.3 Synthesis of $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ (1)

The bulk sample was prepared by dissolving 0.076 g (0.17 mmol) of Hpy3asym and 0.09 g (0.37 mmol) of $Cu(NO_3)_2{\cdot}3H_2O$ in 10 ml of an acetonitrile-water mixture (1:1). The resulting solution was stirred for one hour at room temperature and evaporated till dryness under reduced pressure. After washing with a small amount of acetone, 0.08 g (0.1 mmol, 59% yield) of the pure compound was obtained as a dark green powder. Elemental analysis, % found (calc.) for $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ (=$C_{27}H_{31}Cu_2N_8O_{11.5}$): C, 41.3 (41.7); H, 4.0 (3.9); N, 14,4 (14.7). MS(ESI): *m/z* 688 ($[Cu_2(py3asym)(NO_3)_2]^+$). IR: 3600-3200, broad band (H_2O, asymmetric and symmetric OH stretching), 3184 (N-H stretching), 1613 (HOH bending), 1484 (chelating didentate NO_3^-, N=O stretching), 1396 (monodentate NO_3^-, NO_2 asymmetric stretching), 1290 (monodentate NO_3^-, symmetric NO_2 stretching, and chelating didentate NO_3^-, asymmetric NO_2 stretching).[23]

Single crystals of the complex, suitable for X-ray crystal structure determination, were obtained by slow evaporation of an acetonitrile solution containing stoichiometric amounts of $Cu(NO_3)_2 \cdot 3H_2O$ and the ligand.

2.3.4 X-ray crystallographic measurements

A single crystal of $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_{2.5}](NO_3)_{0.5}$ was mounted at 100 K on a Bruker AXS SMART 6000 diffractometer equipped with Cu-Kα radiation (λ = 1.54184 Å). $C_{27}H_{31}Cu_2N_8O_{11.5}$, Fw = 778.68 g mol^{-1}, rectangular green needles, 0.17×0.08×0.07 mm^3, a = 10.3731(2) Å, b = 22.1430(4) Å, c = 14.2325(2) Å, β =105.709(10)°, Z = 4, V = 3146.98(9) $Å^3$, $\rho_{calc.}$ = 1.644 g cm^{-3}, μ = 2.322 cm^{-1}, absorption correction: SADABS,[24] monoclinic, space group $P2_1/n$ (no. 14), reflections collected: 18421, independent reflections: 5871 (R_{int} = 0.0314). The structure was solved by direct methods and refined using the SHELX program package.[25,26] All hydrogen atoms were placed on idealized positions riding on the carrier atom, with isotropic thermal parameters, except two hydrogen atoms connected to O20. They were assigned to rest electron density on the electron density map. The final cycle refinement, including 475 parameters, converged to *R1* = 0.0312 (*R1* = 0.0388 all data) and *wR2* = 0.0800 (*wR2* = 0.0826 all data) with a maximum (minimum) residual electron density of 0.463 (–0.293) e $Å^{-3}$.

Crystallographic data (without structure factors) for the structure of the complex have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 197305. Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; tel: (+44) 1223-336-408; fax: (+44) 1223-336-003).

2.4 References

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