The Dicopper(II) Complex of the Novel Asymmetric Dinucleating Ligand Hpy3asym as a Structural Model of Catechol Oxidase

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The new asymmetric dinucleating ligand 2-{[bis(2-pyridinylmethyl)amino]methyl}-4-methyl-6-{[(2-pyridinylmethyl)amino]methyl}phenol (Hpy3asym) has been designed in order to model the type-3 active site of the copper proteins. This phenol-based "end-off" compartmental ligand has one tridentate and one didentate arm attached to the 2- and 6-positions of the phenolic ring, respectively. A dinuclear copper(II) nitrate complex with this ligand [Cu₂(py3asym)-(H₂O)_{1.5}(NO₃)₂]NO₃ has been obtained and structurally char-

acterized. 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 an N_3O_3 donor set for the Cu1 ion and an N_2O_4 donor set for the Cu2 ion. The electrochemical, magnetic behavior and spectral properties of the complex are discussed.

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Introduction

The copper proteins with the type-3 active site, such as hemocyanins, tyrosinases and catechol oxidases, have attracted the attention of scientists due to their ability to process primary dioxygen under ambient conditions.^[1-3] The latter two enzymes use it to perform selective oxidations of organic substrates, such as tyrosine and catechol, to produce various melanins, whereas hemocyanin is the dioxygen transport and storage protein in some arthropods and molluscs.

The type-3 active site is characterized by a dicopper core where each of the metal ions is surrounded by three histidine residues. In the met-Cu^{II}-Cu^{II} form two copper ions are antiferromagnetically coupled via the μ -OH bridge, resulting in an EPR-silent active site.

The determination of the crystal structure of catechol oxidase from sweet potatoes (*Ipomoea batatas*) by some of us^[4] offered new insight into the catalytic mechanism of the enzyme with the possibly different functions of the two cop-

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Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 8, 48149 Münster, Germany Fax: (internat.) +49-251/833-8366 E-mail: krebs@uni-muenster.de per ions. Taking our inspiration from the natural molecule, our attention has turned to the deliberate design of novel model systems of the type-3 active site, where the two copper ions would have distinctively 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, i.e. is the catechol substrate forming a bridge between the two copper(II) centers rather than binding to only one of them?

Dinucleating phenol-based "end-off" compartmental^[5] ligands have previously been successfully used for modeling dimetallic biosites.^[6-8] In this paper, the synthesis of the novel phenol-based ligand 2-{[bis(2-pyridinylmethyl)amino]methyl}-4-methyl-6-{[(2-pyridinylmethyl)amino]methyl}phenol, Hpy3asym, is reported. This dinucleating ligand was designed to hold two copper ions in close proximity and to provide them with different coordination surroundings, thus making one of the two copper ions more readily accessible for the binding of the substrate. This was achieved by substituting the 2- and the 6-positions of the phenol ring by tridentate and didentate arms, respectively, containing nitrogen donor atoms. The reaction of Hpy3asym with copper(II) nitrate yields the new dinuclear asymmetric complex, which is regarded as a structural model of the type-3 active site. The dinuclear copper core exhibits a donor-atom asymmetry in the solid state, comprised of an N₃O₃ donor set for the Cu1 ion and an N₂O₄ donor set for the Cu2 ion. The crystal structure, spectroscopy, electrochemical and magnetic behavior of the complex are reported below.

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Figure 1. The reaction scheme of the synthesis of the phenol-based compartmental "end-off" ligand Hpy3asym

Results and Discussion

Ligand Design

Hpy3asym was synthesized in three steps (Figure 1) from commercially available 5-methylsalicylaldehyde. The first step includes the introduction of the dichloromethane group in the 3-position of the phenol ring. The chloride atom was subsequently substituted by di(2-picolyl)amine. Finally, the reductive amination of the aldehyde group by 2-aminomethylpyridine and sodium borohydride led to the desired ligand.

Crystal Structure Description

Very small green rectangular crystals of [Cu₂(py3asym)- $(H_2O)_{1.5}(NO_3)_2](NO_3)$ were obtained by slow evaporation of the solvent from an acetonitrile solution of the complex. The Platon^[9] projection of the complex is depicted in Figure 2. The compound crystallizes in the space group $P2_1/n$. Both copper ions have distinctively different coordination surroundings, showing a donor-atom asymmetry. An endogenous phenolato bridge is present in the dinuclear core, but there is no exogenous bridge. The N₃O₃ coordination sphere around the Cu1 ion can be regarded as a very distorted octahedron. The equatorial plane is formed by the *tert*iary 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) A and 1.9760(18) A, respectively, and the oxygen atom 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 counteranion [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.^[10–13] The in-plane *cis* angles around the Cu1 ion vary over quite a broad range, viz. 83.92(8)° for the N1–Cu1–N3 angle and 96.92(7)° for the O2–Cu1–N2 angle. Their sum amounts to 357.76°. The O–Cu1–O angle along the Jahn–Teller axis is equal to 173.85(8)° for the O1–Cu1–O20 angle and 165.46(10)° for the O1–Cu1–O10 angle, thus indicating a significant distortion from a regular octahedral geometry.

The coordination sphere around the second copper ion Cu2 can also be described as a distorted octahedron, but with an N₂O₄ 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) A], N5 from the pyridine ring [the Cu2-N5 distance is 2.0181(17) A], 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) A and 2.5982(16) A, respectively]. The in-plane cis angles vary in the range 87.36°-94.64°. The angle O5-Cu2-O6, which should be equal to 180° in the regular octahedron, is only 157.37(5)°, indicating an even greater distortion from a regular octahedral geometry than observed in the case of the Cu1 ion.



Figure 2. Platon^[9] projection of $[Cu_2(py3asym)(H_2O)_{1.5}-(NO_3)_2]NO_3$; hydrogen atoms are omitted for clarity; the second axial position at Cu1 ion has a O-donor ligand, which was refined to be 50% water and 50% a disordered nitrate anion

The absence of the 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 similar complexes with two types of bridges between the copper ions.^[7,8,14] It is interesting to note 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: 1.5 neutral water molecules are coordinated to the Cu1 ion, whereas two charged nitrate anions are coordinated to the Cu2 ion.

The crystal packing is stabilized by an extensive net of intra- and intermolecular hydrogen bonds (see Table 1). 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 an exogenous pseudobridge between the two copper ions. Furthermore, each formula unit is connected via intermolecular hydrogen bonds to three neighboring units. The Platon^[9] projection of the crystal packing along the crystallographic *a* axis is shown in Figure 3. As can be seen, the molecules are assembled by means of hydrogen bonds to form a "herring bone" pattern.

Physical Characterization

Besides the crystal structure determination, the complex was characterized spectroscopically and magnetically. The electrospray mass spectrum (ESI-MS) of the complex performed in acetonitrile reveals one major peak at m/z = 688, corresponding to $[Cu_2(py3asym)(NO_3)_2]^+$. The theoretical isotope pattern calculated for the empirical formula $C_{27}H_{28}Cu_2N_7O_7$ is in agreement with the experimentally

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Table 1. Hydrogen bonds (D-H···A) with the distance H···A < r(A) + 2.000 Å and the angle DHA > 110°

D-H	d(D-H), Å	d(H···A), Å	<dha>, °</dha>	d(D···A), Å	А
O2-H2a	0.736	1.971	174.09	2.704	011
O2-H2a	0.736	2.518	127.91	3.026	O10
O2-H2a	0.736	2.611	155.96	3.296	N8
O2-H2b	0.915	1.802	154.44	2.657	07
O2-H2b	0.915	2.443	174.95	3.356	N7
O2-H2b	0.915	2.448	145.50	3.245	O6
N4-H4	0.930	2.119	143.16	2.917	O7 ^[a]
N4-H4	0.930	2.574	156.83	3.448	O8 ^[a]
N4-H4	0.930	2.624	156.58	3.497	N7 ^[a]
O20-H20a	0.759	2.087	163.07	2.821	O9 ^[b]
O20-H20b	0.999	2.010	164.96	2.985	O9
O20-H20b	0.999	2.476	145.58	3.348	N8A
O20-H20b	0.999	2.486	127.27	3.191	011



Figure 3. The Platon^[9] projection of the "herring bone" packing arrangement along the crystallographic a axis; all hydrogen atoms, except for those participating in hydrogen bonding, are omitted

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 an LMCT transition between the bridging phenoxo group and copper ions,^[14] whereas the second one is characteristic for Cu^{II} d-d transitions.^[15] 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}/Cu^{II,I} redox couple. The second one, at -0.33 V, is attributed to the formation of Cu^{II,I} species. They both appear to be irreversible. In addition, a very

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broad peak at ca. -0.7 V suggests the reduction of both copper ions to Cu⁰ and the deposition 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 socalled 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 Cu⁰ can 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.

Magnetic Properties

In Figure 4, the magnetic susceptibility of the complex $[Cu_2(py3asym)(H_2O)_{1.5}(NO_3)_2]NO_3$ 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 cm³·K·mol⁻¹. The value for μ is 1.10 B.M.



Figure 4. Magnetic susceptibility plotted as χ^{-1} versus *T* (O) and as χ versus T (\Box); the dashed line is the Curie–Weiss plot from near field theory and the solid line is the theoretical curve according to the Bleany-Bowers equation

The magnetic properties of this dinuclear copper(II) complex have been interpreted in terms of the Bleaney–Bowers equation [Equation (1)], where g is the magnetic field splitting factor, J is the exchange integral of magnetic theory and N_{α} is the temperature-independent paramagnetism of one mol of copper(II) ions.^[16,17]

$$\chi_{M} = \frac{g^{2} N \beta^{2}}{3kT} (1 + \frac{1}{3} e^{J/kT})^{-1} + N\alpha$$
(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 $J = -4.6 \text{ cm}^{-1}$, the magnetic field splitting factor g = 2.02 and $R = 2.9 \times 10^{-3}$.

Conclusion

The asymmetric phenol-based "end-off" compartmental ligand 2-{[bis(2-pyridinylmethyl)amino]methyl}-4-methyl-6-{[(2-pyridinylmethyl)amino]methyl}phenol forms a dinuclear asymmetric copper(II) nitrate complex which can be regarded as a new structural model of the type-3 active site of the copper proteins. The ligand holds a tridentate and a didentate arms attached to the 2- and 6-positions of the phenol ring. In the solid state the complex possesses donoratom asymmetry, constituted by an N₃O₃ donor set for the Cu1 ion bound to a tridentate arm, and an N₂O₄ donor set for the Cu2 ion bound to a didentate arm. The magnetic behavior of the complex was interpreted in terms of weak ferromagnetic coupling between the two copper ions, with the exchange integral J = -4.6 cm⁻¹, and a Curie–Weiss temperature θ of 0.87 K.

Experimental Section

General Remarks: 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-Chloro-5-methylsalicylaldehyde (1) was prepared according to the procedure described by Lock.^[18] Tetrahydrofuran and methanol were dried by refluxing over sodium. Water was demineralized prior to use. C,H,N determinations were performed on a Perkin-Elmer 2400 Series II analyzer. NMR spectra were recorded on a JEOL FX-200 (200 MHz) 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 of pure solids on a Perkin-Elmer FT-IR Paragon 1000 spectrophotometer with a Specac single-reflection diamond ATR P/N 10500, using the diffuse reflectance technique ($4000-300 \text{ cm}^{-1}$, 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 mV/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 magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.^[19]

3-{[Bis(2-pyridinylmethyl)amino]methyl}-2-hydroxybenzaldehyde (2): 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 with stirring to a solution of **1** (1 g, 5.4 mmol) in 250 mL of dry THF under an 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 compound **2** crystallized within a few minutes. Recrystallization from a methanol/diethyl ester mixture gave slightly yellowish crystals of the pure compound **2**. Yield: 1.55 g, 4.5 mmol (82%). ¹H NMR (CDCl₃, 200 MHz): $\delta = 10.42$ (s, 1 H, aldehyde proton),

8.56 (d, 2 H, 6'py-*H*), 7.63 (td, 2 H, 4'py-*H*), 7.40 (t, 2 H, 5'py-*H*), 7.20 (d, 2 H, 3'py-*H*), 7.15 (s, 1 H, 2'phenol-*H*), 7.13 (s, 1 H, 5'phenol-*H*), 3.89 [s, 4 H, N-(*CH*₂py)₂], 3.80 (s, 2 H, phenol-*CH*₂-N), 2.23 (s, 3 H, *CH*₃) ppm.

2-{[Bis(2-pyridinylmethyl)amino]methyl}-4-methyl-6-{[(2-pyridinylmethyl)imino]methyl}phenol (3): A solution of 2-pyridylmethylamine (0.39 g, 3.6 mmol) in 50 mL of dry methanol was added dropwise with stirring to a solution of **2** (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 spectroscopy. The imine was reduced in situ to the respective amine with sodium borohydride. ¹H NMR (CDCl₃, 200 MHz): δ = 8.51 (d, 3 H, 6'py-*H*), 8.34 (s, 1 H, C*H*=N), 7.62 (td, 3 H, 4'py-*H*), 7.33 (t, 3 H, 5'py-*H*), 7.26(d, 2 H, 3'py-*H*), 7.09 (s, 1 H, 3'phenol-*H*), 7.03 (2, 1 H, 5'phenol-*H*), 4.92 (s, 2 H, CH=N-CH₂), 3.88 [s, 4 H, N-(CH₂py)], 3.80 (s, 2 H, phenol-CH₂-N), 2.29 (s, 3 H, CH₃) ppm.

2-{[Bis(2-pyridinylmethyl)amino|methyl}-4-methyl-6-{[(2-pyridinylmethyl)amino|methyl}phenol (Hpy3asym): NaBH₄ (0.41 g,10.9 mmol, 3 equiv./CH=N) was added in situ to a solution of 3 in methanol. After the hydrogen evolution stopped, the resulting colorless solution was refluxed for two hours and the solvent was evaporated under reduced pressure. The residue was dissolved in acidified water and washed three times with dichloromethane. The water layer was made alkaline (pH \approx 9) by addition of concentrated ammonia. The resulting white suspension was extracted three times with dichloromethane. The organic layers were collected and dried over Na₂SO₄. After evaporation under reduced pressure, the pure compound was obtained as a clear yellow oil. Yield: 1.54 g, 3.5 mmol (96%). ¹H NMR (CDCl₃, 200 MHz): $\delta = 8.55$ (d, 3 H, 6'py-H), 7.59 (td, 3 H, 4'py-H), 7.36 (d, 3 H, 3'py-H), 7.14 (t, 3 H, 5'py-H), 6.93 (s, 1 H, 3'phenol-H), 6.84 (s, 1 H, 5'phenol-H), 3.95 (s, 2 H, NH-CH₂-py), 3.91 (s, 2 H, phenol-CH₂-NH), 3.85 [s, 4 H, N(CH₂-py)₂], 3.75 (s, 2 H, phenol-N-CH₂), 2.22 (s, 3 H, CH₃) ppm. ¹³C NMR (CDCl₃, 200 MHz): $\delta = 159.35$, 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 ppm.

[Cu₂(py3asym)(H₂O)_{1.5}(NO₃)₂](NO₃): The bulk sample was prepared by dissolving Hpy3asym (0.076 g, 0.17 mmol) and Cu(NO₃)₂·3H₂O (0.09 g, 0.37 mmol) in 10 mL of an acetonitrile/ water mixture (1:1). The resulting solution was stirred for one hour at room temperature and the solvents evaporated to 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. C₂₇H₃₁Cu₂N₈O_{11.5} (778.68): calcd. C 41.7, H 3.9, N 14.7; found C 41.3, H 4.0, N 14.4. MS(ESI): m/z = 688 ([Cu₂(py3asym)(NO₃)₂]⁺). IR: $\tilde{\nu} = 3600-3200$, broad band (H₂O, asymmetric and symmetric OH stretching), 3184 (N–H stretching), 1613 (HOH bending), 1484 (chelating didentate NO₃⁻, N=O stretching), 1396 (monodentate NO₃⁻, symmetric NO₂ stretching, and chelating didentate NO₃⁻, asymmetric NO₂ stretching).^[20]

Single crystals of the complex, suitable for X-ray crystal structure determination, were obtained by slow evaporation of the solvent from an acetonitrile solution containing stoichiometric amounts of $Cu(NO_3)_2$ ·3H₂O and the ligand.

X-ray Crystallographic Study: A single crystal of $[Cu_2(py3asym)(-H_2O)_{1.5}(NO_3)_2](NO_3)$ was mounted at 100 K on a Bruker AXS SMART 6000 diffractometer equipped with Cu- K_{α} radiation ($\lambda = 1.54184$ Å). $C_{27}H_{31}Cu_2N_8O_{11.5}$, M = 778.68 g mol⁻¹, rectangular

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green needles, $0.17 \times 0.08 \times 0.07$ mm, a = 10.3731(2), b = 22.1430(4), c = 14.2325(2) Å, $\beta = 105.709(10)^\circ$, Z = 4, V = 3146.98(9) Å³, $\rho_{calcd.} = 1.644$ g cm⁻³, $\mu = 2.322$ cm⁻¹, absorption correction: SADABS,^[21] 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.^[22,23] All hydrogen atoms were placed at idealized positions riding on the carrier atom, with isotropic thermal parameters, except for two hydrogen atoms located close to O20. They were assigned to rest electron density on the electron density map. The final cycle refinement, including 475 parameters, converted 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.

CCDC-197305 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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