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Synthesis, structural characterization and catalytic activities of dicopper(II) complexes derived from tridentate pyrazole-based N_2O ligands

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A group of a diverse family of dinuclear copper(II) complexes derived from pyrazole-containing tridentate N_2O ligands, 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (Hdmpzpo), 1,3-bis(3-phenyl-5-methyl pyrazol-1-yl)propan-2-ol (Hpmpzpo) and 1,3-bis(3-cumyl-5-methylpyrazol-1-yl)propan-2-ol (Hcmpzpo), were synthesized and characterized by elemental analysis, IR spectroscopy and three of them also by single-crystal X-ray diffraction. Three complexes, $[Cu_2(pmpzpo)_2](NO_3)_2{\cdot}2CH_3OH$ ($3{\cdot}2CH_3OH$), $[Cu_2(pmpzpo)_2](ClO_4)_2$ (4) and $[Cu_2(cmpzpo)_2](ClO_4)_2{\cdot}2DMF$ ($7{\cdot}2DMF$), each exhibits a dimeric structure with a inversion center being located between the two copper atoms. The metal ion is coordinated in a distorted square planar environment by two pyrazole nitrogen atoms and two bridging alkoxo oxygen atoms. Both complexes $1{\cdot}CH_3OH{\cdot}H_2O$ and $3{\cdot}2CH_3OH$ were investigated in anaerobic conditions for the catalytic oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to the corresponding quinone (3,5-DTBQ), for modeling the functional properties of catechol oxidase.

KEYWORDS: catechol oxidase; dicopper (II) complex; tridentate N_2O ligand; crystal structure; catalytic activity

INTRODUCTION

Copper plays a vital role in biological systems. It is mainly bound in metalloenzymes, being involved in processes like hydroxylation, oxygen transport, electron transfer, and catalytic oxidation.[1–3] Of these copper enzymes catechol oxidase (CO), also known as *o*-diphenol oxidase, is a less well-known member of the type-3 copper proteins, catalyzing exclusively the oxidation of catechols (i.e. *o*-diphenols) to the corresponding quinones.[2] X-ray crystal structural analysis of catechol oxidase was successfully carried out by Krebs and coauthors a few years ago.[4] The analysis revealed that the active site consists of a dinuclear copper (II) center with the two Cu(II) ions being 2.9 Å apart in the oxidized state and, in addition to the six histidine ligands, a bridging hydroxide ion completes the four-coordinate trigonal pyramidal coordination sphere for each Cu(II) ion.

In order to obtain a deeper insight into the mechanism of catechol oxidation by the natural enzyme, as proposed by Krebs and coworkers,[4] and to simulate the properties of the active site of catechol oxidase, numerous N_3 and N_2O ligands and corresponding dicopper (II) complexes were designed, synthesized, structurally characterized and catalytic properties investigated.[1,5–13] For example, $[CuHB(3,5\text{-}i\text{-}Pr^2Pz)_3]_2(O_2)$ was used to model the μ-η^2 : η^2 binding mode of the O_2^{2-} localized between two Cu atoms in *oxy*HC.[1] However, all model compounds synthesized so far have only achieved turnover numbers about 10 000-fold lower than the native enzymes.[5] In 2001, The group of Jan Reedijk designed and synthesized the ligand 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (Hdmpzpo) and its dicopper(II) complexes and investigated the catalytic activities of one complex for the polymerization of 2,6-dimethylphenol (DMP).[14] Inspired by this ligand and the versatility of the

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substituents on the pyrazole ring, we designed and synthesized a series of pyrazole-containing N_2O ligands and their Cu(II), Zn(II), Ni(II) and Co(II) complexes, of which a few Zn(II), Ni(II) as well as one dicopper(II) complex, $[Cu_2(dmpzpo)_2]Br_2{\cdot}2CH_3OH$, have been reported.[15,16] As our continued work, we report herein the syntheses and characterization of a series of novel dicopper(II) complexes derived from three of these ligands (scheme 1) and the catalytic activities of $[Cu_2(dmpzpo)_2](NO_3)_2{\cdot}CH_3OH{\cdot}H_2O$ for the oxidation of 3,5-di-*tert*-butylcatatechol (3,5-DBCT) to the corresponding quinone (3,5-DBCQ) in anaerobic conditions, for modeling one of the functions of the catechol oxidase.

EXPERIMENTAL

Materials and instruments

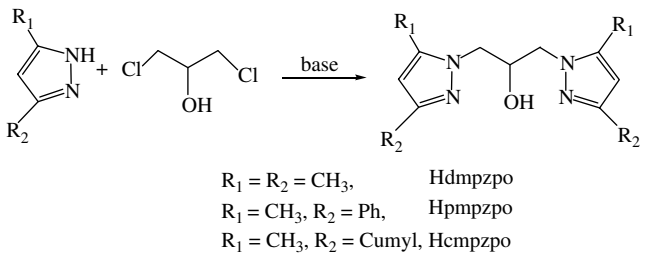
All chemicals and solvents were purchased from commercial sources and used as received, unless stated otherwise. The ligand 1,3-bis (3,5-dimethylpyrazol-1-yl)-propan-2-ol (Hdmpzpo), 1,3-bis (3-phenyl-5-methylpyrazol-1-yl)-propan-2-ol (Hpmpzpo) and 1,3-bis(3-cumyl-5-methylpyrazol-1-yl)propan-2-ol (Hcmpzpo) were designed and synthesized according to Scheme 1; for their detailed synthetic procedures and spectra please refer to our earlier work.[15]

Elemental analysis (C, H, N) was determined with a German Vario EL III instrument. The IR spectrum was recorded from KBr pellets in the range 4000–400 cm^{-1} on an American Thermo Nicolet AVATAR 360FT-IR spectrophotometer. Crystal structures were determined on a Bruker Smart-1000 CCD X-ray diffractionmeter. Catalytic oxidation of the selected catechol was performed on a TU-1901 UV–vis spectrophotometer.

Syntheses of complexes

*$[Cu_2(dmpzpo)_2](NO_3)_2{\cdot}CH_3OH{\cdot}H_2O$, **1**·$CH_3OH{\cdot}H_2O$*

A solution of the ligand Hdmpzpo 0.500 g (2.0 mmol) in 10 ml of methanol was combined with 0.083g (2.0 mmol) sodium hydroxide dissolved in 10 ml of methanol, and stirred for 30 min. Then, the solution was added dropwise to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.483 g, 2.0 mmol) in 10 ml of methanol. The deep blue solution was filtered after an additional 1 h stirring and then evaporated to dryness. The residue was extracted with CH_2Cl_2 in order to remove the remaining reactants. The resulting extract was evaporated and then extracted with CH_3CN and set aside for solvent evaporation. After several days a deep blue powder was collected, filtered, washed with cooled methanol and air-dried. Yield: 0.469 g, 58.0%. $F_w = 794.18$ g mol^{-1}. Anal. calcd for $C_{27}H_{44}Cu_2N_{10}O_{10}$: C, 40.75; H, 5.57; N, 17.60%. Found: C, 40.34; H, 5.027; N, 17.70%. IR(KBr): 1624, 1550 cm^{-1} ($\nu_{C=C/C=N}$), 1384 cm^{-1} ($\nu_{NO3}-$).



Scheme 1. The synthetic route of three pyrazole-based N_2O ligands.

*$[Cu_2(dmpzpo)_2](ClO_4)_2{\cdot}0.5H_2O{\cdot}CH_3CN$, **2**·$0.5H_2O{\cdot}CH_3CN$*

The synthetic procedure was similar to that of **1**·$CH_3OH{\cdot}H_2O$. Here only $Cu(ClO_4)_2{\cdot}6H_2O$ was used instead of $Cu(NO_3)_2{\cdot}3H_2O$, and dark blue powder was afforded. Yield: 0.432 g, 52.6%. $F_w = 869.11$ g mol^{-1}. Anal. calcd for $C_{28}H_{43}Cl_2Cu_2N_9O_{10.5}$: C, 38.58; H, 4.97; N, 14.46%. Found: C, 39.06; H, 5.043; N, 14.20%. IR(KBr): 1682, 1551 cm^{-1} ($\nu_{C=C/C=N}$), 1106, 1075 cm^{-1} ($\nu_{ClO4}-$).

*$[Cu_2(pmpzpo)_2](NO_3)_2{\cdot}2CH_3OH$, **3**·$2CH_3OH$*

A solution of the ligand Hpmpzpo 0. 748 g (2.0 mmol) in 10 ml of THF was mixed with 0.108 g (2.0 mmol) sodium methanoxide dissolved in 10 ml of methanol, and stirred for 30 min. Then, the solution was added dropwise to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0. 483 g, 2.0 mmol) in 10 ml of methanol with stirring. The afforded brown precipitate was stirred for additional 30 min, filtered, washed with THF and air-dried. Yield: 0.893 g, 84.4%. Single crystals suitable for X-ray crystallography analysis were obtained using an H-type glass test tube after several weeks. $F_w = 1014.04$ g mol^{-1}. Anal. calcd for $C_{47}H_{50}Cu_2N_{10}O_9$ (only one methanol molecule is included): C, 54.48; H, 4.97; N, 13.81%. Found: C, 54.48; H, 5.213; N, 13.97%. IR(KBr): 1628, 1552, 1485, 1448 cm^{-1} ($\nu_{C=C/C=N}$), 1380 cm^{-1} ($\nu_{NO3}-$).

*$[Cu_2(pmpzpo)_2](ClO_4)_2$ **4***

The synthetic procedure was similar to that of **3**·$2CH_3OH$. Here only $Cu(ClO_4)_2{\cdot}6H_2O$ was used instead of $Cu(NO_3)_2{\cdot}3H_2O$. Yield: 0.815 g, 76.1%. Single crystals suitable for X-ray crystallography analysis were obtained using an H-type glass test tube after several weeks. $F_w = 1130.18$ g mol^{-1}. Anal. calcd for $C_{48}H_{54}Cu_2N_8O_{12}Cl_2$ (two additional methanol molecules are included): C, 50.88; H, 4.80; N, 9.89%. Found: C, 51.03; H, 4.895; N, 9.77%. IR(KBr): 1633, 1551, 1484, 1448 cm^{-1} ($\nu_{C=C/C=N}$), 1093 cm^{-1} ($\nu_{ClO4}-$).

*$[Cu_2(pmpzpo)_2]Br_2{\cdot}CH_3OH$, **5**·$CH_3OH$*

The synthetic procedure was similar to that of **3**·$2CH_3OH$. Here only $CuBr_2$ was used instead of $Cu(NO_3)_2{\cdot}3H_2O$, and deep-brown precipitate was afforded. Yield: 0.835 g, 81.1%). $F_w = 1058.10$ g mol^{-1}. Anal. calcd for $C_{47}H_{50}Cu_2N_8O_3Br_2$: C, 53.16; H, 4.75; N, 10.55%. Found: C, 52.98; H, 4.42; N, 10.75%. IR(KBr): 1632, 1549, 1490, 1446 cm^{-1} ($\nu_{C=C/C=N}$).

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*[Cu_2(cmpzpo)$_2$](NO_3)$_2$·2CH_3OH, **6**·2CH_3OH*

The synthetic procedure was similar to that of **3**·2CH_3OH, only ligand Hcmpzpo was employed to substitute for the ligand Hpmpzpo. The green solution was set aside for evaporation at room temperature and a green powder was obtained. Yield: 0.635 g, 51.8%. $F_w = 1226.4$ g mol^{-1}. Anal. calcd for $C_{60}H_{78}Cu_2N_{10}O_{10}$: C, 58.76; H, 6.41; N, 11.42%. Found: C, 58.48; H, 6.173; N, 11.39%. IR(KBr): 1622, 1555, 1519, 1448 cm^{-1} ($\nu_{C=C/C=N}$), 1380 cm^{-1} (ν_{NO3}−).

*[Cu_2(cmpzpo)$_2$](ClO_4)$_2$·2DMF, **7**·2DMF*

The synthetic procedure was similar to that of **6**·2CH_3OH, only $Cu(ClO_4)_2$·6H_2O was used instead of $Cu(NO_3)_2$·3H_2O, and a brown precipitate was obtained. Yield: 0.635 g, 51.8%. Single crystals suitable for X-ray crystallography analysis were obtained using an H-type glass test tube after several weeks. $F_w = 1383.4$ g mol^{-1}. Anal. calcd for $C_{64}H_{84}Cu_2N_{10}O_{12}Cl_2$: C, 55.56; H, 6.12; N, 10.12%. Found: C, 55.90; H, 6.218; N, 9.932%. IR(KBr): 1616, 1554, 1522, 1452 cm^{-1} ($\nu_{C=C/C=N}$), 1091 cm^{-1} (ν_{ClO4}−).

*[Cu_2(cmpzpo)$_2$]Br_2, **8***

The synthetic procedure was similar to that of **6**·2CH_3OH, only $CuBr_2$ was used instead of $Cu(NO_3)_2$·3H_2O, The deep green solution was set aside for evaporation at room temperature and a deep green powder was afforded. Yield: 0.749 g, 62.5%. $F_w = 1198.1$ g mol^{-1}. Anal. calcd for $C_{58}H_{70}Cu_2N_8O_2Br_2$: C, 58.14; H, 5.89; N, 9.35%. Found: C, 58.12; H, 6.233; N, 9.65%. IR(KBr): 3030, 1631, 1555, 1522, 1445, 791 cm^{-1}.

Crystal structure determination

The determination of the unit cell and the data collection for the complexes **3**·2CH_3OH, **4** and **7**·2DMF were performed on a Bruker Smart-1000 CCD diffractionmeter with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using ω-2θ scan technique. The structures were solved by direct methods using SHELXS-97[17,18] and refined against F^2 by full matrix least-squares using SHELXL-97.[17,18] All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction study showed no decomposition during data collection. A summary of the crystal data, experimental details and refinement results is given in Table 1. Selected bond lengths and angles of complexes **3**·2CH_3OH, **4** and **7**·2DMF are listed in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 646306 (**3**·2CH_3OH), 646307 (**4**) and 646308 (**7**·2DMF). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ,

Table 1. Crystallographic data for complexes **3**·2CH_3OH, **4** and **7**·2DMF

Compound	**3**·2CH_3OH	**4**	**7**·2DMF
Chemical formula	$C_{48}H_{54}Cu_2N_{10}O_{10}$	$C_{46}H_{46}Cl_2Cu_2N_8O_{10}$	$C_{64}H_{84}Cl_2Cu_2N_{10}O_{12}$
Formula weight	1058.09	1068.89	1383.39
Temperature(K)	298(2)	273(2)	298(2)
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/n
Crystal size	0.38 × 0.21 × 0.18	0.18 × 0.15 × 0.11	0.41 × 0.39 × 0.24
Crystal color	Brown	Brown	Brown
Crystal description	Block	Block	Block
a (Å)	11.017(6)	10.1581(16)	11.892(7)
b (Å)	15.143(9)	14.399(17)	15.774(9)
c (Å)	14.90(8)	15.7485(16)	18.397(10)
β (deg)	95.788(8)	92.7840(10)	90.749(9)
V (Å^3)	2474(2)	2300.8(5)	3451(3)
Z	2	2	2
D_{calc}(g cm^{-3})	1.420	1.543	1.331
F(000)	1100	1100	1452
θ min., max	2.394, 26.846	1.92, 25.1	2.02, 25.02
$h/k/l$ range	−12, 13/−14, 18/−17, 17	−12, 12/−17, 16/−18, 11	−14, 12/−16, 18/−21, 21
Reflection measured	12468	11606	17762
Unique reflections(R_{int})	4342[R(int) = 0.1125]	4085[R(int) = 0.0297]	6071[R(int) = 0.1065]
Final R indicices	$R_1 = 0.0696$, $wR_2 = 0.1780$	$R_1 = 0.0401$, $wR_2 = 0.1067$	$R_1 = 0.0805$, $wR_2 = 0.2001$
R indices (all data)	$R_1 = 0.1129$, $wR_2 = 0.2122$	$R_1 = 0.0555$, $wR_2 = 0.1142$	$R_1 = 0.1427$, $wR_2 = 0.2633$
Min. and max. residual density (e Å^{-3})	−1.063, 0.947	−0.302, 0.476	−0.738, 0.869

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Table 2. Selected bond lengths (Å) and angles (deg) for complexes **3**·2CH_3OH, **4** and **7**·2DMF

3·2CH_3OH		**4**		**7**·2DMF	
Cu(1)···Cu(1)A	2.988 (2)	Cu(1)···Cu(1)A	2.999 (8)	Cu(1)···Cu(1)A	2.997 (2)
Cu(1)···O(1)	1.910 (3)	Cu(1)···O(1)	1.900 (2)	Cu(1)···O(1)	1.906 (5)
Cu(1)···O(1)A	1.905 (4)	Cu(1)···O(1)A	1.902 (2)	Cu(1)···O(1)A	1.913 (5)
Cu(1)···N(1)	1.950 (4)	Cu(1)···N(1)	1.956 (2)	Cu(1)···N(1)	1.940 (6)
Cu(1)···N(3)A	1.942 (4)	Cu(1)···N(3)A	1.950 (2)	Cu(1)···N(3)A	1.957(6)
N(1)···Cu(1)···N(3)A	103.79(19)	N(1)···Cu(1)···N(3)A	103.69(10)	N(1)···Cu(1)···N(3)A	103.3(2)
O(1)···Cu(1)···O(1)A	76.88(16)	O(1)···Cu(1)···O(1)A	75.83(9)	O(1)···Cu(1)···O(1)A	76.6(2)
O(1)···Cu(1)···N(1)	90.31(17)	O(1)···Cu(1)···N(1)	91.06(9)	O(1)···Cu(1)···N(1)	89.9(2)
O(1)A···Cu(1)···N(1)	164.08(18)	O(1)A···Cu(1)···N(1)	163.28(10)	O(1)A···Cu(1)···N(1)	165.2(2)
O(1)···Cu(1)···N(3)A	164.32(18)	O(1)···Cu(1)···N(3)A	163.42(10)	O(1)···Cu(1)···N(3)A	165.7(2)
O(1)A···Cu(1)···N(3)A	90.20(17)	O(1)A···Cu(1)···N(3)A	90.85(9)	O(1)A···Cu(1)···N(3)A	90.7(2)
Cu(1)···O(1)···Cu(1)A	103.12(16)	Cu(1)···O(1)···Cu(1)A	104.17(9)	Cu(1)···O(1)···Cu(1)A	103.3(2)

Symmetry codes for **3**·2CH_3OH: A at $1-x, 1-y, -z$; for 4: A at $-x, -y+1, -z$; for **7**·2DMF: A at $x, 2-y, 1/2+z$.

UK (Fax: +44-1223-336-033; e-mail:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

General procedure for the oxidation of 3,5-DTBC

The 1.0×10^{-3} M complex **1**·CH_3OH·H_2O and 1.0×10^{-2} M 3,5-DTBC solutions were prepared with P_2O_5-predried CH_3CN and bubbled with dinitrogen for at least 10 min and kept in septum-sealed volumetric flasks. An 0.8 ml aliquot of the dicopper complex solution (0.4 ml of **1**·CH_3OH·H_2O introduced in the molar ratio of [Cu2] : [3,5-DTBC] = 1 : 50) was taken in a septum-sealed quartz cuvette and 3,5-DTBC solution and acetonitrile were quickly added under dinitrogen atmosphere, with the help of airtight syringes; the total volume of the solution in the quartz cuvette was always maintained at 2.5 ml. Electronic spectra were recorded in different time intervals at room temperature on a TU-1901 UV–vis spectrophotometer.

RESULTS AND DISCUSSION

Crystal structures of complexes 3·2CH_3OH, 4 and 7·2DMF

Since these three complexes are structurally similar in their cation parts, only the structure of the complex **3**·2CH_3OH is described in detail. Their structures are also similar to those reported in the literature.[5–12]

Complex **3**·2CH_3OH crystallizes in the monoclinic system, with space group P2(1)/n. The structure determination revealed that the cation of **3**·2CH_3OH contains a dinuclear copper center in which the metal atoms are coordinated by two ligand molecules. A crystallographic inversion center is located between the two copper atoms so that they are structurally equivalent (Fig. 1). The Cu···Cu distance of 2.988 Å is comparable to the two Cu(II) ions apart in the oxidized state of the natural enzyme and to the Cu···Cu distances in other model compounds.[1,12] Both copper centers are equivalent in the same coordination environment and so have only one type of metal configuration. Each copper atom is coordinated in a distorted square planar geometry by two pyrazole nitrogen atoms and two bridging alkoxo oxygen atoms. The Cu···O and Cu···N bond distances [average Cu···O = 1.908(4) and Cu···N = 1.946(4)Å] are comparable to those of other dicopper complexes.[11,12] The deviation from a regular square is due to the steric force of the chelating ligand, which is induced by the phenyl groups on the pyrazole rings. Thus the two pyrazole rings of one ligand are folded to the back while the pyrazole rings of the other ligand are folded to the front. According to the symmetry, the two copper atoms and the two alkoxo oxygen atoms form an exact Cu_2O_2 plane. One of the two coordinating nitrogen atoms lies above this plane, and the other one below it. The distances from the plane are 0.3038(N3) and 0.3252(N1) Å, respectively, less than those in complexes [Cu_2bbp_2](ClO_4)$_2$·2MeOH.[12] The six-membered chelate rings formed by the ligands have a twisted conformation. Moreover, there exist different types of hydrogen bonds in the molecule: one is the O···H···O intramolecular hydrogen bond between oxygen atom of the ligand anion molecule and the oxygen atom of the methanol molecule, with the angles of 147° [O(5)···H(5)···O(2)] and 138° [O(5)···H(5)···O(4)], respectively; the another one is the intermolecular hydrogen bond between the oxygen atoms of the NO_3^- molecules and the carbon atoms of the propyl and pyrazol-1-yl groups of the ligand molecule, with angles of between 152 and 164°. All these hydrogen bonds link up the complex units and result in a three-dimensional network, making the whole network structure system stable.

The complex **4** crystallizes in the monoclinic system with space group P2(1)/c. The structure of the cation moiety is completely similar to that of **3**·2CH_3OH. One of the two coordinating nitrogen atoms with the metal ions lies above the Cu_2O_2 plane, the other one below it, with the distances from

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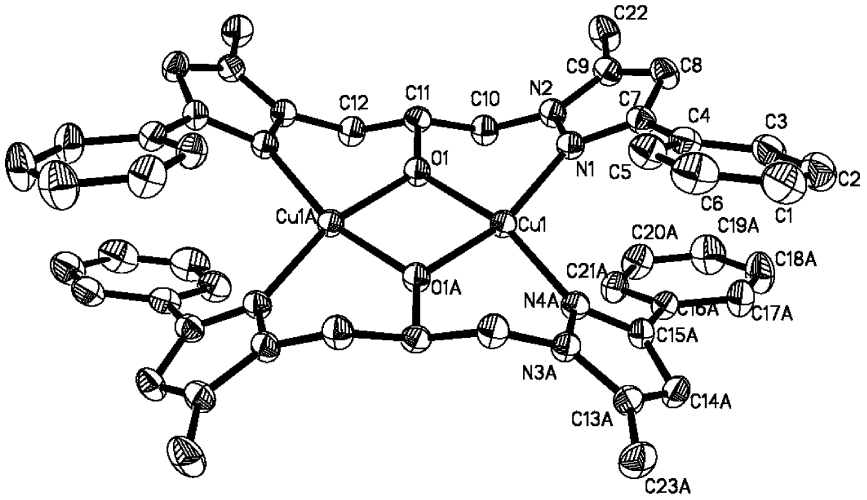

Figure 1. Molecular structure and atomic numbering scheme for the cation of $[Cu_2(pmpzpo)_2](NO_3)_2{\cdot}2CH_3OH$, **3**·$2CH_3OH$. Hydrogen atoms are omitted for clarity.

the plane being 0.3564 (N1) and 0.3386 (N4) Å, respectively. There exists intermolecular C···H···O hydrogen bonding between the oxygen atoms of the perchlorate anion molecules and the carbon atoms of the ligands as well.

The complex **7**·2DMF crystallizes in the monoclinic system, with space group P2(1)/n, similar to that of **3**·$2CH_3OH$. The structure of it, as shown in Fig. 2, is again similar to that of **3**·$2CH_3OH$. Each copper metal is again coordinated by two nitrogen atoms of pyrazole rings and two oxygen atoms of the bridging alkoxo groups, forming a distorted square planar coordination geometry. Like those in the structures of two complexes mentioned above, one of the two coordinating nitrogen atoms lies above the Cu_2O_2 plane and the other one below it, with the distances being 0.2095 (N2) and 0.2283 (N3) Å, respectively, which are considerably shorter than those in two complexes mentioned above. There exists a certain degree of disorder in the counterion ClO_4^-. In addition, rich hydrogen bonds in the complex extend the molecules into multiple-dimensional network.

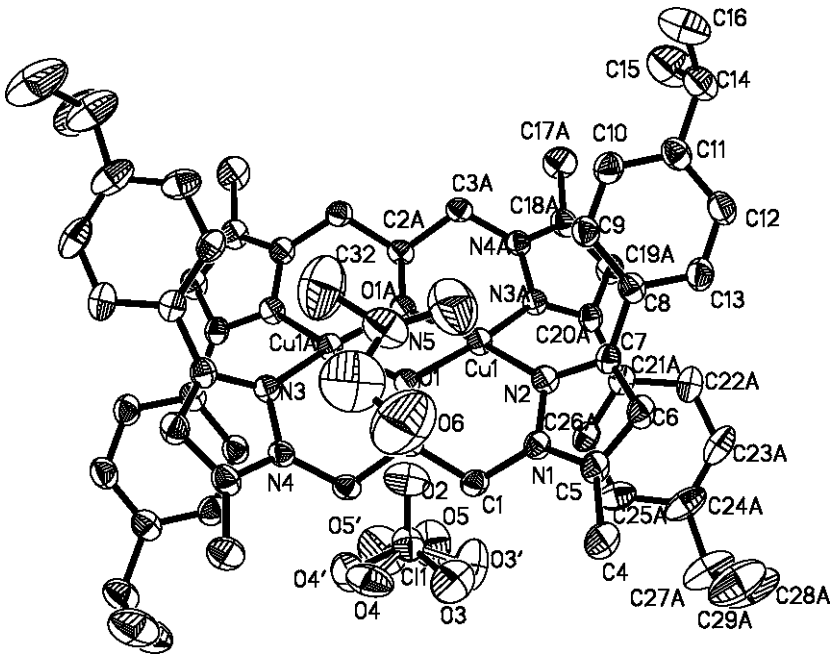

Figure 2. Molecular structure and atomic numbering scheme for complex $[Cu_2(cmpzpo)_2](ClO_4)_2{\cdot}2DMF$, **7**·2DMF. Hydrogen atoms are omitted for clarity.

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Catechol oxidase model studies

Among the different catechols used in catechol oxidase model studies, 3,5-DTBC is the most widely used substrate due to its low redox potential for the quinone–catechol couple, which makes it easily oxidized to the corresponding quinone 3,5-DTBQ, and its bulky substituents, which make further oxidation reactions such as ring opening slower. The detection of the oxidation of 3,5-DTBC to the corresponding 3,5-DTBQ can be followed by the development of the adsorption band at about 400 nm ($\varepsilon = 1900\ M^{-1}\ cm^{-1}$; MeOH).[19,20] The reduction of Cu(II) to Cu(I) was followed by observing the decrease in the optical density of the band centered in the range of 600–700 nm.

For compound $[Cu_2(dmpzpo)_2](NO_3)_2{\cdot}CH_3OH{\cdot}H_2O$, **1**·$CH_3OH{\cdot}H_2O$, at $[Cu_2]$:[3,5-DTBC] stoichiometry of 1 : 5, as shown in Fig. 3, the band at 400 nm increased in intensity with the reaction time at room temperature, indicative of the formation of 3,5-DTBQ and the successive increment of its concentration. Simultaneously the band at 625 nm decreased in intensity with time, indicating that the Cu^{2+} species was destroyed and the band at 350 nm, attributed to the π(pyrazole) → Cu(II) LMCT transitions, decreased in intensity and finally vanished, indicative of the formation of Cu(I). When the $[Cu_2]$:[3,5-DTBC] stoichiometry was lowered from 1 : 5 to 1 : 10 to 1 : 20 for the compound **1**·$CH_3OH{\cdot}H_2O$, as can be seen from Fig. 4, the quinone absorption at 400 nm increased in intensity with the lowering of the molar ratio of $[Cu_2]$: [3,5-DTBC], and when the $[Cu_2]$:[3,5-DTBC] molar ratio was lowered further to 1 : 50, the intensity of the absorption of 3,5-DTBQ decreased, as observed in the catalytic oxidation investigations of the copper complexes employed in the group of Jan Reedijk.[21] In all investigations, it was found that the catalytic reaction was finished after 1 h, indicative of the much lower activity of our employed dicopper complexes on comparison with the reported dicopper complexes earlier,[6,20] their catalytic oxidation being generally finished within a few minutes at low catechol to complexes ratios. The reason for this observation can be tentatively ascribed to the stereo effects of the ligands we employed in this work, and our initial investigations on the catalytic activity of the complex $[Cu_2(pmpzpo)_2]Br_2{\cdot}CH_3OH$, with more bulky substituents at the 3-position of the pyrazolyl rings, strengthened this assumption. It was also found that eventually the color of the solutions faded from initial bluish to brownish yellow, strengthening the assertion that the copper(II) complexes are reduced to copper(I) complexes.

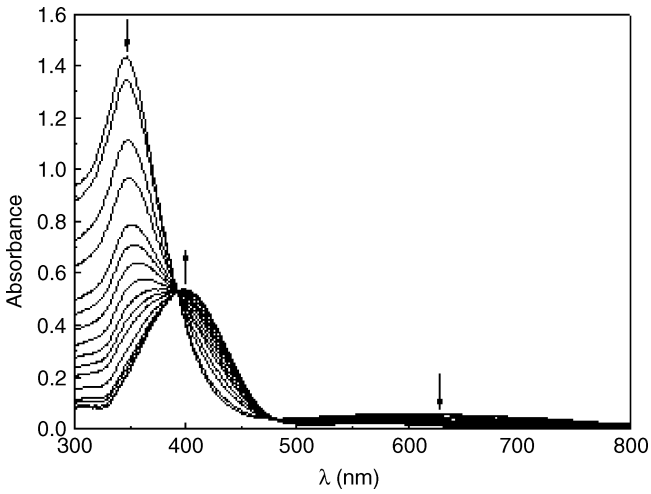

Figure 3. The 3,5-DTBQ formation with the time due to aerobic oxidation of 3,5-DTBC in the presence of complex **1**·$CH_3OH{\cdot}H_2O$ ($c_{int.} = 3.2 \times 10^{-4}$ mol l^{-1} and molar ratio of $[Cu_2]$: [3,5-DTBC] = 1:5).

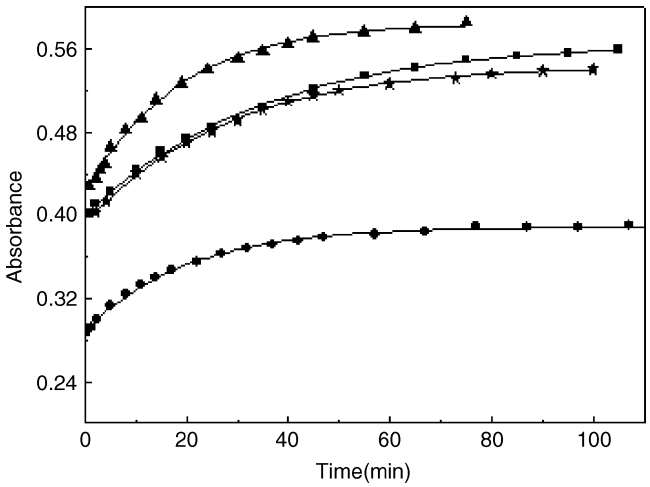

Figure 4. Plot of absorbance vs time for aerobic oxidation of 3,5-DTBC in the presence of complex **1**·$CH_3OH{\cdot}H_2O$ with molar ratio of $[Cu_2]$: [3,5-DTBC] = 1:5 (asterisks), 1 : 10 (squares), 1 : 20 (triangles) and 1 : 50 (circles).

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