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Synthesis and Structure of a Binuclear Cu(II) Complex of 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol

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Abstract: The synthesis and crystal structure of Cu(II) complex of a binucleating tridentate ligand 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol (**I**) is being reported. The two chelating bispicolylamine arms in **I** are tethered by a 2-hydroxypropyl group with Cu(II) coordinating in a slightly distorted square planar geometry to give $[Cu_2(\mathbf{I})(OH_2)(Cl)](ClO_4)_3 \cdot 2H_2O$ (**II**). The crystal data for **II**: Triclinic, space group $P\bar{1}$ with cell dimensions of a = 13.345 (4) Å, b = 13.873 (4) Å, c = 12.867 (2) Å, α = 111.68 (2)°, β = 100.34 (2)°, γ = 65.83 (2)°, V = 2018.4 (9) Å^3, *F.W.* = 962.46, ρ_{calc} = 1.583 g cm^{-3} for Z = 2, μ = 13.93 cm^{-1}

Keywords: Cu(II) complex, bispicolylamine, 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol

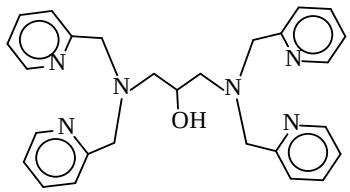
1. Introduction

The fact that many enzymes require metal ions to achieve full catalytic activity has stimulated interest on the chemistry taking place at the active sites of the metalloenzymes [1-4]. Model enzymes are being developed and extensive studies conducted in order to gain an understanding of the factors underlying the relationship between coordination geometry and the nature of the donor ligands. For example, copper(II) complexes coordinated to polydentate pyrazole-based ligands have been proposed as models for the type 3 copper proteins [5-7]. Copper-containing proteins are involved in various essential bio-processes and amongst them are *hemocyanin*, which binds and transports O_2, *tyrosinase* which has a catecholase and cresolase activity, and *catechol oxidase* for the oxidation of catechols [8,9]. A striking feature of the type 3 copper proteins is that they contain binuclear Cu(II) centres in

their active sites with each centre coordinated by three hystidine nitrogen atoms [10-12]. It is for this reason that nitrogen donor ligands such as pyridine and pyrazole are a logical choice in modelling of copper proteins since the former have pKa values that are close to those found in histidyl moieties in several enzymes [13,14].

Karlin et al.[15], for example, were able to demonstrate that the binuclear Cu (I) complex of m-xylpy (py = 2-pyridyl) acts as a good model for the deoxy-sites in the proteins. Selmeczi et al.[16] also reported the syntheses of dicopper complexes of 1,3-bis{N,N-bis(2-[2-pyridyl]ethyl)amino}propane and 1,3-bis{N,N-bis(2-[2-pyridyl]ethyl)amino}-2-hydroxypropane and were able to demonstrate their ability to catalyze the oxidation of 3,5-di-*tert*-butylcatechol as well as highlight some of the fundamental structure-reactivity relationships.

Previously we reported the syntheses and X-ray structures of Zn(II) complexes of bis(2-pyridylmethyl)amine (bpa), bis(2-pyridyl-2-ethyl)amine (bpea), 2,2′-dipyridylamine (dipyam) and 2,2′-dipyridyl (dipy) in an attempt to develop complexes that could mimic the structure and function of the active sites of zinc enzymes such as alkaline phosphatase and carbonic anhydrase [17]. The catalytic behaviour on the hydrolysis of bis(4-nitrophenyl)phosphate by these zinc complexes were subsequently determined. In this paper we report the synthesis and characterisation of a Cu(II) complex of 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol (**I**) with a view to understanding the coordination behaviour of the binucleating tridentate N-donor ligands.



1,3-bis(bispicolylamino)-2-propanol

(**I**)

2. Experimental

2.1. Materials

Methanol, methylene chloride, acetonitrile, $Cu(ClO_4)_2 \cdot 6H_2O$, 2-picolylchloride·HCl, 1,3-diamino-2-hydroxypropane and NaOH were reagent grade and were used as purchased from Aldrich. The ligand 1,3-bis (bispicolylamino)-2-propanol was synthesized by a modification of literature method and characterized by spectroscopic methods. ^{1}H-NMR spectra were run in deuterated solvents with internal TMS standard on a *GE* 300 MHz spectrometer. IR spectra were collected on a Perkin-Elmer FT-IR. UV-Vis spectra were collected on a Perkin-Elmer Lambda 2 spectrometer using 1-cm quartz cuvettes. The %Cu in a complex was determined using Perkin-Elmer AAS (model 2380) equipped with a hollow cathode source and employing air/acetylene flame.

2.2 Synthesis of 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol

The ligand 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol (**I**) was synthesized by a slight modification of the literature method [18]. An aqueous solution of NaOH (0.091 mol in 40 cm^3 water) was added dropwise to an aqueous solution of 2-picolylchloride·HCl prepared by adding 15.0 g of 2-picolylchloride·HCl (0.091 moles) to 40 cm^3 of distilled water at 0 ^oC. An aqueous solution of 1,3-diamino-2-hydroxypropane (2.05 g in 40 cm^3 water), also maintained at 0 ^oC, was added dropwise to the vigorously stirred reaction mixture. The mixture was stirred for 20 min after which 200 cm^3 of methylene chloride was added. The reaction mixture, maintained at pH 9-10, was left to stir for 2 days at 0 ^oC and for 4 more days at room temperature. The solution was then extracted with three 60 cm^3 portions of methylene chloride. The combined methylene chloride extracts were dried with anhydrous $MgSO_4$. Methylene chloride was removed by means of a rotary evaporator to yield 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol (**I**) as a brown oil (65% yield). ^1H NMR($CDCl_3$-TMS): δ(ppm): 2.68 (m,4H), 3.88 (s,8H), 5.29 (d,1H), 7.11 (m,4H), 7.38 (m,4H), 7.58 (m,4H), 8.49 (m,4H)

2.3 Synthesis of $[Cu_2(I)(OH_2)(Cl)](ClO_4)_3·2H_2O$

To a solution of 1.0g (2.2 mmol) of 1,3-bis(bispicolylamino)-2-propanol in 75 cm^3 water:methanol (1:9) was added 1.63g (4.4 mmol) of $Cu(ClO_4)_2·6H_2O$. The mixture was allowed to stir at room temperature for 24 h followed by slow refluxing for another 24 h. The solvent was allowed to evaporate slowly at room temperature resulting in blue crystals of $[Cu_2(\mathbf{I})(OH_2)(Cl)](ClO_4)_3·2H_2O$ complex **II**. IR (Nujol), υ (cm^{-1}): 3500.0 (OH stretch), 1613 (NH stretch), 1575.0 (pyridyl stretch), 1066.8 (ClO_4^-), UV-Vis: λ_{max} = 669 nm, ε_{max} = 134.57 $M^{-1}cm^{-1}$, % Cu: found = 13.31, calc = 13.36

2.4 Crystallographic structure determination

A crystal of complex **II** was mounted in a random orientation on the end of a glass fiber using 5 min epoxy cement and transferred to a goniometer head. Preliminary crystal parameters and reflection data were obtained at room temperature and processed by standard methods [19,20] on a Rigaku AFC6S X-ray diffractometer with graphite monochromated Mo K_α radiation and 12 kW rotating anode generator. Details of the crystal data collection are given in Table 1. The structure was solved by direct methods [21] as implemented in the SHELXTLPC system of computer programmes and refined to convergence by full matrix least-squares methods. All hydrogens were found and their positional parameters refined. Atomic scattering factors used were those from the International Table for X-ray crystallography [22].

Table 1. Crystallographic data for $[Cu_2(I)(OH_2)(Cl)](ClO_4)_3 \cdot 2H_2O$ (II)

Chemical formula	$C_{27}H_{36}N_6O_{16}Cl_4Cu_2$	α(°)	*111.68(2)*
Formula weight	969.46	β(°)	*100.34(2)*
Crystal colour, habit	Blue, prism	γ(°)	*65.85(2)*
Crystal system	Triclinic	V(Å^3)	*2018.4(9)*
Crystal dimensions	0.400x0.300x0.500	Z	*2*
Space group	$P\bar{1}$	D_{calc}(g/cm^3)	*1.583*
a(Å)	13.345(4)	μ(Mo Kα), cm^{-1}	*13.93*
b(Å)	13.873(4)	No unique reflections	*9250*
c(Å)	12.867(2)	No of observations	*3805*
		R	*0.081*
		R_w	*0.101*

$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$ $\quad R_w = [(\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2)]^{½}$

Table 2. Selected bond distances an bond angles for $[Cu_2(I)(OH_2)(Cl)]^{2+}$

Bond distance (Å)

Cu1–CL1	2.247 (3)	Cu2–O1W	1.974 (8)
Cu1–N1A	2.000 (9)	Cu2–N1B	2.003 (9)
Cu1–N2A	2.028 (8)	Cu2–N2B	2.027 (8)
Cu1–N3A	1.967 (9)	Cu2–N3B	1.970 (1)

Bond angles (°)

CL1–Cu1–N1A	97.9 (2)	O1W–Cu2–N1B	96.8 (4)
CL1–Cu1–N2A	178.0 (3)	O1W–Cu2–N2B	174.4 (4)
CL1–Cu1–N3A	96.5 (3)	O1W–Cu2–N3B	97.8 (4)
N1A–Cu1–N2A	84.0 (3)	N1B–Cu2–N2B	83.4 (3)
N1A–Cu1–N3A	164.3 (3)	N1B–Cu2–N3B	163.5 (3)
N2A–Cu1–N3A	81.6 (4)	N2B–Cu2–N3B	82.8 (4)

Estimated standard deviations in the least significant figure are given in parentheses

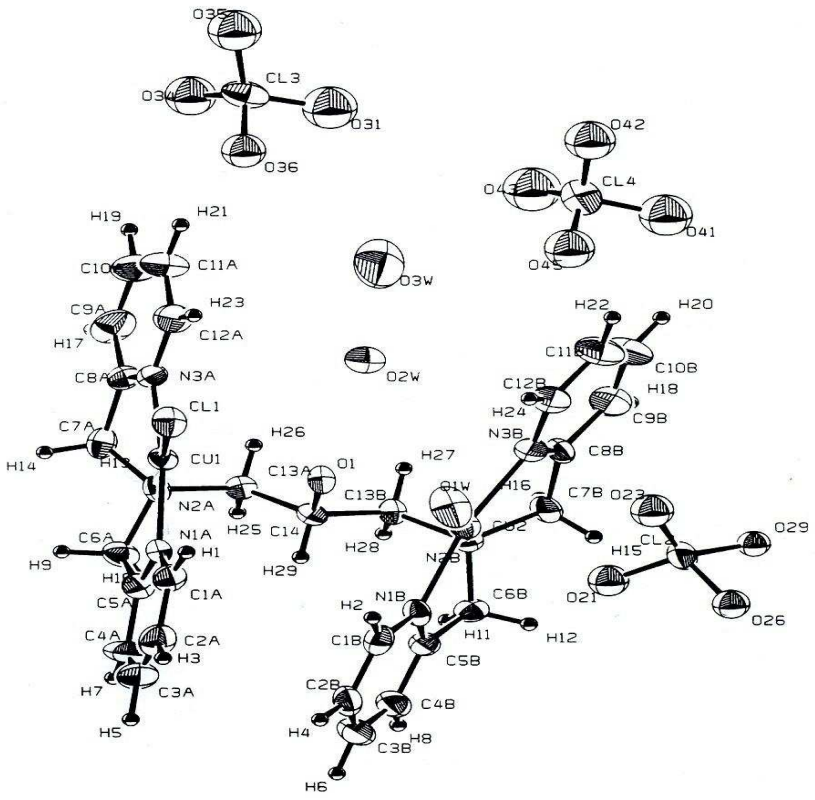


Figure 1. Ortep drawing of the crystal structure of $[Cu_2(\mathbf{I})(OH_2)(Cl)]^{2+}$, the cation of complex **II**

3. Results and Discussion

The reaction of **I** with two equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ gave a binuclear Cu complex **II**. A summary of the crystallographic data and structure parameters for **II** is provided in Table 1. A list of selected bond distances and bond angles is given in Table 2. The ORTEP drawing of the crystal structure for $[Cu_2(\mathbf{I})(Cl)(OH_2)]^{2+}$, the cation of complex **II,** is shown in Figure 1. The two chelating bispicolylamine arms are tethered by a 2-hydroxypropyl group with each Cu^{2+} ion coordinated to three bispicolylamine nitrogen atoms, a H_2O molecule on one arm and Cl ligand on the other arm with the latter produced *in situ* from the dissociation of metal perchlorate [23]. In the outer coordination sphere there are three perchlorate anions and two water molecules of crystallization. The bonds CL1-Cu1-N2A and N1A-Cu1-N3A have bond angles of 178.0 and 164.3 respectively which are close to 180 ^oC. The bond angles in CL1-Cu1-N1A (97.9), CL1-Cu1-N3A (96.5), N1A-Cu1-N2A (84.0), N2A-Cu1-N3A (81.6) are close to 90^o. This suggests a slightly distorted square planar geometry around Cu1 ion. The bonds O1W-Cu2-N2B and N1B-Cu1-N3B have bond angles of 174.4 and 163.5 respectively which are close to 180 ^oC. The bond angles in O1W–Cu2–N1B (96.8), O1W-Cu2-N3B (97.8), N1B-Cu2-N2B (83.4.0), N2B-Cu2-N3B (82.3) are all close to 90^o. This also suggests a slightly distorted square planar geometry around Cu2 ion. The bispicolylamine arms chelate to Cu^{2+} centres with Cu-N bond distances of 1.967(9)^o, 1.970(1)^o, 2.000(9)^o, 2.003(9)^o, 2.027(8)^o, 2.028(8)^o, Cu-CL bond distance of 2.247(3)^o and Cu-O bond distance of 1.974(8)^o. The Cu-N and Cu-O bond distances in **II** are typical

and compares closely to those in a dicopper complex of 1,3-bis{N,N-bis(2-[2-pyridyl]ethyl)amino}propane [14]. The latter has been shown to catalyse the oxidation of 3,5-di-tert-butylcatechol to the corresponding *o*-quinone and hydrogen peroxide.

4. Conclusions

A dicopper complex of 1,3-bis [N,N-bis(2-picolyl)amino]propan-2-ol has been prepared and its structure characterised by IR, UV, AA, ^{1}H-NMR and X ray diffraction. An investigation of this complex as a model for the active sites of copper–containing enzymes with binuclear Cu(II) centres is soon to follow.

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