Cu(I)–Dioxygen Reactivity: Structural Characterization of a Bridged-Binuclear Cu(II) Complex Formed by Oxidation of a New Binuclear Cu(I) Compound

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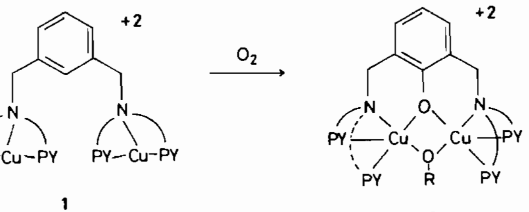
We are involved in investigations of the coordination chemistry and reactivity of nitrogen ligand containing mono- and bi-nuclear copper(I) complexes. These are of interest because of their relevance to the active site chemistry of certain redox active copper metalloenzymes. The proteins include the oxygen carrier hemocyanin [1], the monooxygenases tyrosinase and dopamine beta-hydroxylase [2], and the 'type 3' copper centers found in the multicopper blue oxidases [1, 3]. All of these proteins are important in biological reactions involving dioxygen, and it is established that it is the reduced state of copper which interacts with dioxygen in these systems.

We recently reported a novel reaction involving a binuclear copper complex of the binucleating ligand *meta*-XYLpy2 (py2 = bis(2-(2-pyridyl)ethyl)amine). The three-coordinate binuclear Cu(I) complex *1* reacts with O_2, resulting in oxygenation of the xylyl containing binucleating ligand and concomitant formation of phenoxy-bridged binuclear Cu(II) complexes *2* [4]. This reactivity closely resembles the action of the copper monooxygenases with respect to the coordination chemistry of the binuclear copper complexes and in the stoichiometry of reaction.



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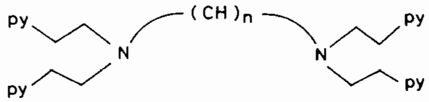
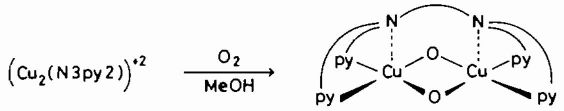
To better understand the coordination requirements involved in Cu(I)–O_2 activation, we have extended our studies to involve the ligands Nnpy2 (n = 3, 4, 5), possessing a variable methylene chain connecting the two py2 tridentate units which coordinate to each copper ion. Marked differences in reactivity may be expected by variation of the connecting group in Nnpy2 [5]. The present studies are aimed at elucidating the effects upon the Cu(I)–O_2 reactivity of a) altering the extent of metal–metal interaction (by changing n) and b) changing from an aryl group (XYL) to a less reactive alkyl group in the proximity of the copper ions. Here, we report the synthesis and characterization of the ligand N3py2 (n = 3), its binuclear Cu(I) complex, *3*, and the reactivity of the latter with dioxygen. $Cu_2(N3py)^{+2}$, *3*, reacts with O_2 giving rise to a new class of bridged binuclear Cu(II) complexes; we have characterized a dimethoxy bridged derivative by x-ray crystallography.



Nnpy2



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The ligand N3py2 was prepared by the reaction of excess 2-vinyl pyridine with 1,3-propane diamine in methanol (acetic acid catalyst). Purification was effected by chromatography on silica gel in methanol–water. The complex $[Cu_2{}^I(N3py2)](ClO_4)_2$, *3*, was isolated as a yellow powder by reaction of two equivalents of $Cu(CH_3CN)_4ClO_4$ with N3py2 in THF-Acetone under argon. This binuclear Cu(I) complex was reacted with dioxygen as a suspension in MeOH to give a blue-green solution. Precipitation with Et_2O and recrystallization from MeOH–Et_2O afforded the crystalline complex $[Cu_2(N3py2)(OMc)_2](ClO_4)_2$*, *4*.

$[Cu_2(N3py2)(OMe)_2](ClO_4)_2$ crystallizes in the monoclinic space group $P2_1/m$ with a = 8.182(4), b = 13.912(7), c = 17.245(6) Å, β = 93.20(4)°, V = 1959.8 Å^3, and Z = 2. A total of 1234 reflections were refined to obtain the current residual values of R = 0.0899 and R_w = 0.0942. (MoKα, $\bar{\lambda}$ = 0.71069 Å).

The structure (Fig. 1) consists of a discreet binuclear complex with two tetragonally coordinated Cu(II) ions bridged in the equitorial positions by the methoxy ligands. The Cu_2O_2 bridging unit is rigorously planar; the two copper atoms are related by a crystallographic mirror plane containing O1, O2, C4

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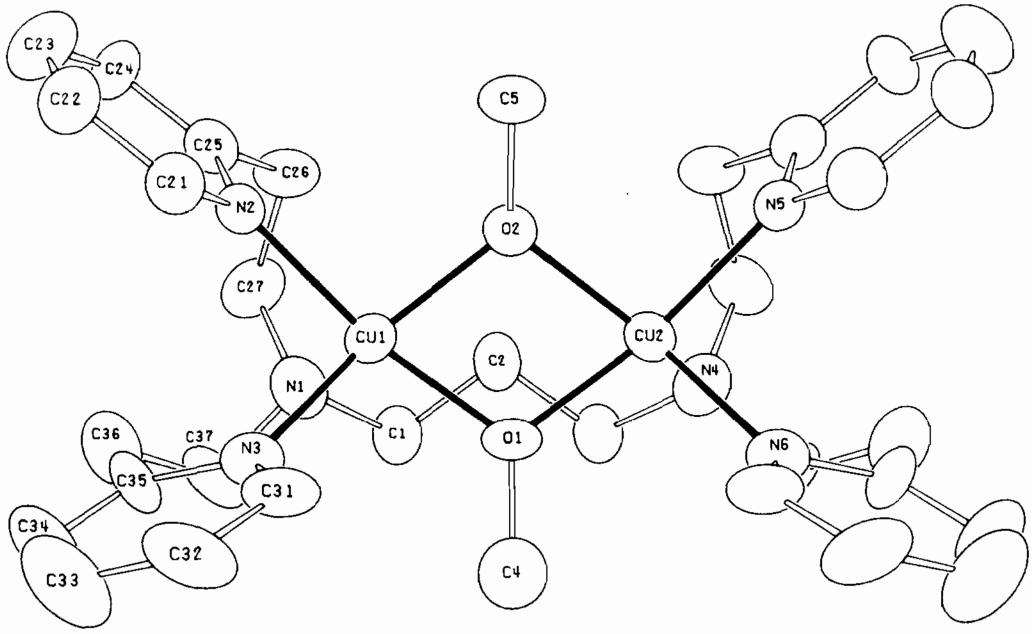

Fig. 1. ORTEP of the $[Cu_2(N3py2)(OMe)_2]^{+2}$ dication, *4*, showing the atom labelling scheme. Selected bond lengths (Å) and angles (deg) are Cu...Cu, 3.070; Cu1–O1, 1.934(9); Cu1–O2, 1.934(8); Cu1–N1, 2.363(13); Cu1–N2, 1.992(12); Cu1–N3, 2.004(14); N1–Cu1–N2, 89.0(5); N1–Cu1–N3, 91.7(6); N1–Cu1–O1, 101.7(6); N1–Cu1–O2, 115.3(5); N2–Cu1–N3, 89.8(5); N2–Cu1–O1, 168.4(6); N2–Cu1–O2, 96.8(5); N3–Cu1–O1, 94.1(5); N3–Cu1–O2, 152.2(6); O1–Cu1–O2, 74.8(5); Cu1–O1–Cu2, 105.0(6); Cu1–O2–Cu2, 105.0(7); Cu1–O1–C4, 127.4(3); Cu1–O2–C5, 124.9(5).

TABLE I. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å $\times 10^3$).

Atom	x	y	z	U equiv/iso
Cu(1)	9161(2)	3603(1)	7520(1)	46(1)*
O(1)	8952(19)	2500	8190(8)	51(5)*
O(2)	9541(17)	2500	6872(8)	51(5)*
N(1)	6457(15)	4206(10)	7438(8)	61(5)*
N(2)	9774(17)	4602(9)	6761(6)	54(5)*
N(3)	9803(22)	4499(7)	8395(9)	64(5)*
C(1)	5347(21)	3387(11)	7617(10)	64(6)*
C(2)	5523(30)	2500	7180(15)	70(10)*
C(4)	8589(33)	2500	8967(16)	77(11)*
C(5)	10563(37)	2500	6211(13)	75(10)*
C(21)	11283(17)	5060(9)	6885(6)	59(6)*
C(22)	11720(17)	5803(9)	6394(6)	81(8)*
C(23)	10649(17)	6087(9)	5779(6)	104(10)*
C(24)	9141(17)	5629(9)	5655(9)	78(8)*
C(25)	8703(17)	4886(9)	6146(6)	59(6)*
C(26)	7176(21)	4325(14)	6042(10)	69(7)*
C(27)	5965(21)	4621(13)	6661(11)	72(7)*
C(31)	11284(22)	4251(7)	8784(9)	76(8)*
C(32)	12140(22)	4929(7)	9243(9)	120(12)*
C(33)	11515(22)	5856(7)	9313(9)	124(13)*
C(34)	10035(22)	6105(7)	8924(9)	117(12)*
C(35)	9179(22)	5426(7)	8465(9)	83(8)*
C(36)	7630(23)	5685(14)	8031(12)	83(8)*
C(37)	6281(22)	4930(14)	8066(10)	72(7)*
Cl(1)	4211(9)	2500	145(5)	95(4)*
Cl(2)	4694(9)	2500	4544(5)	81(3)*
O(11)	2577(37)	2500	260(15)	161(15)
O(11′)	4601(87)	2500	881(43)	275(36)
O(12)	4961(63)	1508(31)	64(27)	304(18)
O(21)	6457(35)	2500	4750(15)	180(12)
O(21′)	3733(76)	2500	5075(35)	212(25)
O(22)	4214(48)	2093(25)	3826(19)	277(18)
O(22′)	4662(53)	1477(32)	4578(23)	163(23)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ii} tensor.

and C5 of the methoxy groups as well as C2 of the connecting methylene chain in N3py2. The other two positions in the basal plane of the copper ions are taken by pyridine nitrogen ligands. Long axial interactions (Cu–N = 2.363(13) Å) occur from the tertiary amino nitrogen atoms of the py2 ligating group. The Cu...Cu distance is 3.070(2) Å which is normal for doubly -OR bridged Cu(II) dimers [6] and compares closely to that found for the phenolate bridged complexes, *2* [4a, 7].

As has been previously suggested [8], formation of this methoxy bridged species may result from MeOH attack on oxygen intermediates formed by the reaction of $Cu_2(N3py2)^{+2}$ with O_2. We also observe that if the reaction of *3* with dioxygen is carried out in CH_2Cl_2, the corresponding di-hydroxy bridged complex $[Cu_2(N3py2)(OH)_2]^{+2}$, *5*, is formed*. Thus,

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*Satisfactory elemental analyses have been obtained for all binuclear copper complexes.

TABLE II. Bond Lengths (Å).

Cu(1)–O(2)	1.934(9)	Cu(1)–N(2)	1.992(12)
Cu(1)–N(3)	2.004(14)	Cu(1)–N(1)	2.363(13)
Cu(1)–O(1)	1.934(8)	O(2)–C(5)	1.451(30)
O(2)–Cu(2)	1.934(9)	O(21)–Cl(2)	1.466(29)
Cl(2)–O(21′)	1.240(64)	Cl(2)–O(22′)	1.424(44)
O(11)–Cl(1)	1.363(32)	Cl(2)–O(22)	1.398(34)
C(24)–C(25)	1.395	O(12)–Cl(1)	1.520(44)
C(22)–C(21)	1.395	Cl(1)–O(11′)	1.291(74)
C(24)–C(23)	1.395	C(23)–C(22)	1.395
N(2)–C(25)	1.395	C(25)–C(26)	1.475(22)
C(34)–C(33)	1.395	C(34)–C(35)	1.395
C(33)–C(32)	1.395	C(32)–C(31)	1.395
C(31)–N(3)	1.395	N(3)–C(35)	1.395
C(35)–C(36)	1.480(25)	C(37)–C(36)	1.528(27)
C(37)–N(1)	1.491(23)	C(27)–C(26)	1.552(26)
C(27)–N(1)	1.493(24)	N(1)–C(1)	1.500(21)
O(1)–C(4)	1.388(30)	O(1)–Cu(2)	1.934(8)
C(2)–C(1)	1.457(21)	C(2)–C(3)	1.457(21)
C(21)–N(2)	1.395	Cu(2)–O(1)	1.934(8)

no oxygenation of the binucleating ligand occurs from the reaction of *3* with O_2. This also appears to be true of other similar binuclear Cu(I) complexes [8, 9], and it seems that the hydroxylation reaction found in the conversion of *1* to *2* is unique. Studies are in progress to elucidate those factors necessary for the activation of dioxygen (as for *1*) and to understand the mechanism of formation of *4* and *5*.

The phenolate bridged binuclear complexes *2* and related derivatives [7] all possess axial ligation to the two Cu(II) ions from opposite sides of the Cu_2O_2 bridging plane. Here, in *4*, the axial interactions occur on the same side of the corresponding plane. This results in a 'pocket' forming between the Cu_2O_2 plane and the alkyl methylene chain which connects the two py2 units in the N3py2 ligand (see Fig. 1). Here, the binucleating ligand conformation may be of use in studies involving binding of small molecules to this 'protected' side of the copper plane. Axial interaction with potential substrates may also be possible on the open side of the Cu_2O_2 plane, as has been proposed for the hydroxylation of phenols at the binuclear copper active site in tyrosinase [10]. Investigations of these kinds are in progress. The effects of n upon the coordination chemistry and reactivity studies of both Cu(I) and Cu(II) derivatives of Nnpy2 and related ligands are also being pursued.

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TABLE III. Bond Angles (deg.).

O(2)–Cu(1)–N(2)	96.8(5)	O(2)–Cu(1)–N(3)	152.2(6)
N(2)–Cu(1)–N(3)	89.8(5)	O(2)–Cu(1)–N(1)	115.3(5)
N(2)–Cu(1)–N(1)	89.0(5)	N(3)–Cu(1)–N(1)	91.7(6)
O(2)–Cu(1)–O(1)	74.8(5)	N(2)–Cu(1)–O(1)	168.4(6)
N(3)–Cu(1)–O(1)	94.1(5)	N(1)–Cu(1)–O(1)	101.7(6)
Cu(1)–O(2)–C(5)	124.9(5)	Cu(1)–O(2)–Cu(2)	105.0(7)
C(5)–O(2)–Cu(2)	124.9(5)	O(21)–Cl(2)–O(22′)	90.6(18)
O(21)–Cl(2)–O(21′)	118.5(30)	O(21′)–Cl(2)–O(22)	119.6(30)
O(21′)–Cl(2)–O(22′)	87.5(17)	O(12)–Cl(1)–O(11)	114.7(19)
O(21)–Cl(2)–O(22)	116.1(19)	O(11)–Cl(1)–O(11′)	92.8(35)
O(22′)–Cl(2)–O(22)	68.0(21)	C(23)–C(24)–C(25)	120.0
O(12)–Cl(1)–O(11′)	90.6(22)	C(23)–C(22)–C(21)	120.0
C(24)–C(23)–C(22)	120.0	Cu(1)–N(2)–C(21)	118.1(4)
C(22)–C(21)–N(2)	120.0	O(2)–Cu(2)–O(1)	74.8(5)
Cu(1)–N(2)–C(25)	121.8(4)	C(21)–N(2)–C(25)	120.0
C(24)–C(25)–N(2)	120.0	C(24)–C(25)–C(26)	124.2(8)
N(2)–C(25)–C(26)	115.7(8)	C(33)–C(34)–C(35)	120.0
C(34)–C(33)–C(32)	120.0	C(33)–C(32)–C(31)	120.0
C(32)–C(31)–N(3)	120.0	Cu(1)–N(3)–C(31)	113.1(5)
Cu(1)–N(3)–C(35)	123.9(4)	C(31)–N(3)–C(35)	120.0
C(34)–C(35)–N(3)	120.0	C(34)–C(35)–C(36)	120.7(9)
N(3)–C(35)–C(36)	119.3(9)	C(36)–C(37)–N(1)	109.7(15)
C(35)–C(36)–C(37)	114.4(15)	C(26)–C(27)–N(1)	111.4(14)
C(25)–C(26)–C(27)	110.2(14)	Cu(1)–N(1)–C(37)	108.9(10)
Cu(1)–N(1)–C(27)	113.3(10)	C(37)–N(1)–C(27)	111.0(12)
Cu(1)–N(1)–C(1)	107.0(9)	C(37)–N(1)–C(1)	106.3(13)
C(27)–N(1)–C(1)	110.0(12)	Cu(1)–O(1)–C(4)	127.4(3)
Cu(1)–O(1)–Cu(2)	105.06(6)	C(4)–O(1)–Cu(2)	124.4(3)
C(1)–C(2)–C(3)	115.7(22)	N(1)–C(1)–C(2)	117.3(16)

TABLE IV. Anisotropic Temperature Factors ($Å^2 \times 10^3$).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	39(1)	48(1)	51(1)	−4(1)	7(1)	2(1)
O(1)	64(10)	60(9)	31(8)	0	9(7)	0
O(2)	43(9)	54(9)	58(9)	0	14(7)	0
N(1)	33(7)	57(9)	94(10)	−4(8)	16(7)	9(7)
N(2)	50(8)	44(8)	71(9)	1(7)	26(7)	3(6)
N(3)	51(9)	61(9)	80(10)	−8(8)	18(8)	−4(8)
C(1)	56(11)	58(11)	78(11)	12(9)	23(9)	23(8)
C(2)	48(16)	96(21)	66(16)	0	14(13)	0
C(4)	65(18)	74(18)	96(20)	0	34(16)	0
C(5)	108(23)	70(16)	53(15)	0	49(15)	0
C(21)	43(10)	47(10)	88(12)	2(10)	9(9)	−2(9)
C(22)	49(11)	50(12)	144(19)	−5(12)	16(12)	−5(9)
C(23)	107(18)	86(16)	116(17)	60(14)	−1(15)	8(15)
C(24)	93(16)	57(11)	83(13)	36(11)	7(12)	21(12)
C(25)	42(9)	56(11)	80(12)	−11(10)	3(9)	10(8)
C(26)	54(11)	85(14)	69(11)	2(11)	5(9)	6(10)
C(27)	45(10)	79(13)	95(14)	23(11)	23(10)	6(9)
C(31)	82(14)	86(14)	61(11)	−1(11)	4(11)	−21(12)
C(32)	59(13)	187(28)	114(18)	−52(19)	−9(13)	−53(17)
C(33)	103(21)	131(23)	140(22)	−70(20)	28(18)	−1(18)
C(34)	139(23)	74(15)	139(22)	−63(15)	26(19)	−2(16)
C(35)	110(17)	59(13)	84(14)	−22(11)	35(13)	−14(12)
C(36)	61(12)	74(13)	113(15)	−25(12)	−3(11)	28(11)
C(37)	59(11)	86(13)	74(12)	−34(11)	18(10)	3(11)
Cl(1)	48(4)	146(8)	91(6)	0	14(4)	0
Cl(2)	60(4)	82(5)	101(6)	0	8(4)	0

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12})$

TABLE V. Hydrogen Coordinates ($\times 10^4$) and Temperature Factors ($Å \times 10^3$).

Atom	x	y	z	U equiv/iso
H(1a)	5558	3234	8156	84
H(1b)	4233	3595	7531	84
H(2a)	6601	2500	6986	82
H(2b)	4722	2500	6751	82
H(4a)	9601	2482	9276	89
H(4b)	7944	1946	9079	89
H(4c)	7996	3072	9085	89
H(5a)	11656	2310	6375	117
H(5b)	10583	3134	5992	117
H(5c)	10123	2056	5827	117
H(21)	12020	4864	7308	78
H(22)	12758	6118	6480	95
H(23)	10950	6598	5441	116
H(24)	8403	5825	5232	91
H(31)	11713	3612	8736	89
H(32)	13158	4758	9511	115
H(33)	12104	6323	9629	150
H(34)	9606	6743	8972	142

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