

**Molecular Structure of a Binuclear Copper(II) Complex:
[Cu₂L₂DMF₂]·DMF·2ClO₄ (LH = 4-Methyl-2,6-bis(indazol-2-ylmethyl)phenol)**

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The molecular structure of a binuclear copper(II) complex [Cu₂L₂DMF₂]·DMF·2ClO₄ in which LH is 4-methyl-2,6-bis(indazol-2-ylmethyl)phenol and DMF is *N,N*-dimethylformamide is reported. The structure of the crystal was characterized by X-ray diffraction: monoclinic, space group P2₁/c, Z = 2, a = 15.863(4), b = 20.642(3), c = 19.598(5) Å, β = 113.05(2)°. The final R and R_w values are 0.060 and 0.061, respectively, for 4777 reflections with I > 2σ(I). Each copper(II) is penta coordinate, with two N atoms from the indazole ring, two O atoms from phenolate in ligands and another O atom from DMF to form a distorted square-pyramid. The mean value of the lengths of the four Cu-N bonds is 1.987(6) Å and the Cu···Cu distance is 3.094(1) Å. No EPR signal was detected, and the magnetic moment has a small value μ = 1.17 per copper. These results indicate strong antiferromagnetic interaction between the two copper(II) ions.

INTRODUCTION

Binuclear copper complexes containing a copper-ion center and phenolate bridging are extensively investigated because of their structural, magnetic, EPR and spectral properties.¹⁻⁵ Such ligands are designed as models of the active site of type-III copper proteins.⁶⁻¹⁰ Our previous work concerned the metal complexation of bifunctional N atom donor sites of a phenolate bridging ligand and properties of those complexes. We report here the synthesis of the ligand 4-methyl-2,6-bis(indazol-2-ylmethyl)phenol (1) and the structure and properties of its dicopper complex 2.

EXPERIMENTAL SECTION

Physical Methods

Melting points (Thomas-Hoover capillary apparatus) are uncorrected. ¹H NMR spectra were recorded (Bruker AM-200WB instrument) at 200 MHz using CDCl₃ as solvent. Mass spectra were recorded on a Finnigan MAT TSQ-46C instrument, and infrared spectra on a Perkin-Elmer 983G spectrometer with KBr as support. Elemental analysis was done using a Hitachi CHN-O-Rapid Analyzer instrument. The absorption spectra were obtained with a diode-array spectrometer (Hewlett-Packard 8452A) using DMF as solvent. EPR spectra were recorded (Bruker ESP 300 instrument) with diphenylpicrylhydrazyl (dpph) as standard.

Magnetic susceptibility was measured using the Faraday method (CAHN 2000 instrument) with Hg[Co(SCN)₄] as standard, and diamagnetic corrections were made using Pascal's parameters.

Synthesis of 4-Methyl-2,6-bis(indazol-2-ylmethyl)phenol (1)

Indazole (2.36 g, 20 mmol) and triethylamine (5 mL) were dissolved in chloroform (20 mL). Then 4-methyl-2,6-bis(chloromethyl)phenol (2.05 g, 10 mmol) in chloroform (20 mL) was added to the solution. After reflux for 5 h, the solvents were removed under reduced pressure and the residue was washed with acetone. The product was purified by column chromatography (silica gel 60) using ethyl acetate-hexane (1:4) (R_f = 0.3) to give a white solid: mp 158-159 °C (yield, 1.83 g, 50%); Anal. Calcd for C₂₃H₂₀N₄O: C, 74.98; H, 5.47; N, 14.63, Found: C, 74.72; H, 5.59; N, 14.64. MS m/z 368, 250; ¹H NMR (CDCl₃) δ 2.17 (3H, s, arylCH₃), 5.50 (4H, s, arylCH₂N), 6.97 (2H, s, arylH), 7.03-7.73 (8H, m, indazolylH), 8.01 (2H, s, indazolylC³-H).

Synthesis of [Cu₂L₂DMF₂]·DMF·2ClO₄ (2)

Copper(II) perchlorate hexahydrate (371 mg, 1 mmol) and LH (368 mg, 1 mmol) were dissolved in DMF (20 mL) and filtered at room temperature. Deep blue crystals were obtained by slow diffusion of diethyl ether into this mixture: Anal. Calcd for C₅₅H₅₉Cl₂Cu₂N₁₁O₁₃: C, 51.60; H, 4.64; N, 12.03%. Found: C, 50.63; H, 4.61; N, 11.62. IR ν_{max}

3121(m), 1657(s), 1625(m), 1515(m), 1463(m), 1233(m), 1087(s), 761(s), 624(m) cm^{-1} .

Structural Determination

The intensity data for suitable crystals of the complex were collected at 298 K on a CAD-4 diffractometer using monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). The unit-cell parameters were derived from a least-squares refinement of 25 reflections. The θ - 2θ scan technique and a variable scan speed were used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurement and the variation of the intensities was a total decay of 8% in the complex. Absorption corrections were applied according to the experimental Ψ rotation curve. Other details of crystal data are given in Table 1. Selected bond distances and angles are reported in Table 2. The structure was solved by the heavy-atom method. The atomic parameters were obtained from the subsequent Fourier syntheses and the least-squares refinement. The final results of the non-hydrogen are given in Table 3. A crystal-weighting scheme of the form $1/[\sigma^2(F_o) + 0.0001(F_o)^2]$ was used. All the hydrogen-atom parameters were calculated according to the ideal geometry and were not refined. The structural analyses were carried out on Microvax III using NRCVAX programs.¹¹ Atomic scattering factors were taken from the literature.¹²

RESULTS AND DISCUSSION

The ligand 4-methyl-2,6-bis(indazol-2-ylmethyl)phenol (**1**) was prepared as follows. Chloromethylation¹³ of 4-cresol gave 4-methyl-2,6-bis(chloromethyl)phenol; then we treated it with indazole in chloroform and triethylamine to give the ligand. The ligand reacted with copper perchlorate to give the dicopper complex **2** (see Scheme I). Data of the crystalline compound appear in Table 1. Selected bond distances and angles and final atomic parameters are shown in Tables 2 and 3 respectively. The molecular structure is shown in Fig. 1. The dimeric unit has no symmetry at the center of the molecule. Each copper(II) center is coordinated by five donors, two nitrogen atoms from the indazolyl ring of the ligand, two bridging oxygen atoms from phenolate and a non-bridging oxygen atom from DMF. The geometry at each copper(II) center is best described as a distorted square pyramid.¹⁴ As indicated in Fig. 1, the basal plane involves N(1), N(5), O(1) and O(2) for Cu(1) center and N(4), N(7), O(1), and O(2) for Cu(2) center. Two oxygen atoms O(3) and O(4) occupy the apical positions. The Cu(1) is 0.142(3) \AA above the plane containing N(1), N(5), O(1) and O(2) toward the O(3) atom, while the Cu(2) is 0.071(3) \AA above the plane containing N(4), N(7), O(1) and O(2) toward the O(4) atom. There are four seven-membered rings around two copper ions and the torsion angles Cu(2)-

Scheme I

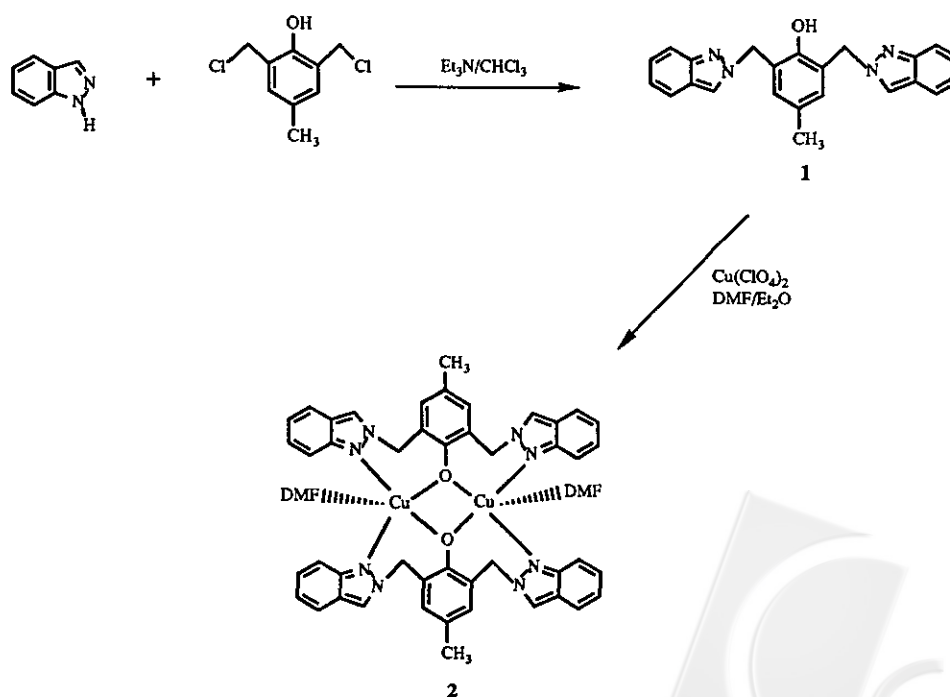


Table 1. Crystallographic Data of the Complex 2

Formula	[Cu ₂ L ₂ (DMF) ₂] ₂ ·2ClO ₄ ·DMF
M/g mol ⁻¹	1280.1
Crystal size/mm ³	0.40 × 0.40 × 0.50
Crystal	Monoclinic
Space group	P2 ₁ /c
a/Å	15.863(4)
b/Å	20.642(3)
c/Å	19.598(5)
β/deg	113.05(2)
V/Å ³	5905.1(22)
Z	4
F(000)	2647
Dc/Mg m ⁻³	1.440
μ/mm ⁻¹	0.88
2θ range/deg	2-45
Ranges of h, k, l	-17 - 15, 0 - 22, 0 - 21
Scan parameters:	1.6 + 0.7 tanθ
Total number of reflections:	7686 (4777 > 2σ)
R, Rw	0.060, 0.061
S	2.54

N(7)-N(8)-C(39) 17.5(3), Cu(1)-N(5)-N(6)-C(31) 31.3(3), Cu(1)-N(1)-N(2)-C(8) 23.2(3) and Cu(2)-N(4)-N(3)-C(16) 25.5(3) indicate that each of the four seven-membered rings is roughly close to be a boat conformation.

The four Cu-N distances are distinct; the Cu(1)-N(5) distance 1.999(6) Å is larger than the other Cu-N distances. The two DMF molecules with a cis arrangement differ from the complex [Cu₂(C₂₄H₂₆N₄O₂)Br₂] of the Robson type.⁴ The Cu(1)···Cu(2) distance is 3.094(1) Å is shorter than

Table 3. Final Atomic Positional Parameters of Non-hydrogen Atoms in the Complex 2

	x	y	z	Beq*
Cu1	0.13782(6)	0.11326(5)	0.23103(5)	3.35(5)
Cu2	0.30739(6)	0.07981(5)	0.19686(5)	3.63(5)
N1	0.1100(4)	0.1165(3)	0.3211(3)	4.2(4)
N2	0.1288(4)	0.0650(3)	0.3683(3)	4.5(4)
N3	0.4886(4)	0.1147(3)	0.3073(3)	4.6(4)
N4	0.4392(4)	0.0687(3)	0.2581(3)	3.8(4)
N5	0.0050(4)	0.1227(3)	0.1660(3)	3.2(3)
N6	-0.0228(4)	0.1702(3)	0.1146(3)	3.5(3)
N7	0.3275(4)	0.0563(3)	0.1058(3)	3.4(4)
N8	0.2816(4)	0.0071(3)	0.0610(3)	3.3(3)
N9	0.2222(6)	0.3084(4)	0.3342(5)	8.9(6)
N10	0.2778(7)	0.2747(4)	0.0955(6)	10.2(8)
O1	0.2682(3)	0.09292(24)	0.27922(24)	3.4(3)
O2	0.1736(3)	0.09097(23)	0.14780(23)	3.2(3)
O3	0.1830(5)	0.2223(3)	0.2511(4)	7.8(5)
O4	0.3276(4)	0.1894(3)	0.1704(3)	5.6(4)
C1	0.0463(6)	0.1527(4)	0.3356(4)	4.7(5)
C2	0.0007(6)	0.2092(4)	0.3006(5)	5.6(6)
C3	-0.0640(7)	0.2342(5)	0.3227(6)	7.5(7)
C4	-0.0839(7)	0.2043(6)	0.3800(6)	9.6(8)
C5	-0.0380(7)	0.1501(6)	0.4169(6)	8.5(8)
C6	0.0283(6)	0.1232(5)	0.3937(5)	5.8(6)
C7	0.0824(6)	0.0682(5)	0.4131(4)	5.5(5)
C8	0.1980(6)	0.0188(4)	0.3699(4)	4.4(5)
C9	0.2914(5)	0.0498(4)	0.3993(4)	3.6(4)
C10	0.3457(6)	0.0438(4)	0.4741(4)	5.0(5)
C11	0.4298(6)	0.0732(4)	0.5061(4)	4.9(5)
C12	0.4925(6)	0.0643(5)	0.5874(5)	6.8(6)
C13	0.4574(5)	0.1122(4)	0.4608(4)	4.6(5)
C14	0.4034(5)	0.1200(4)	0.3853(4)	3.8(4)
C15	0.3198(5)	0.0873(4)	0.3531(4)	3.7(4)
C16	0.4408(5)	0.1584(4)	0.3378(4)	4.3(5)
C17	0.5788(5)	0.1030(5)	0.3345(5)	5.7(6)
C18	0.5901(5)	0.0476(5)	0.3002(5)	5.2(5)
C19	0.6680(7)	0.0129(5)	0.3087(6)	7.5(7)
C20	0.6573(6)	-0.0410(6)	0.2693(6)	8.2(7)
C21	0.5660(7)	-0.0644(5)	0.2189(6)	7.7(7)
C22	0.4893(6)	-0.0285(5)	0.2130(5)	5.7(6)
C23	0.5018(6)	0.0279(4)	0.2533(4)	4.1(4)
C24	-0.0725(5)	0.1047(4)	0.1753(4)	3.5(4)
C25	-0.0835(5)	0.0567(4)	0.2215(4)	3.8(4)
C26	-0.1698(6)	0.0492(4)	0.2213(5)	4.9(5)
C27	-0.2433(5)	0.0874(5)	0.1776(5)	5.4(5)
C28	-0.2346(5)	0.1341(4)	0.1313(5)	5.1(5)
C29	-0.1471(5)	0.1423(4)	0.1302(4)	3.8(4)
C30	-0.1113(5)	0.1830(4)	0.0917(4)	4.2(5)
C31	0.0406(5)	0.1907(4)	0.0809(4)	3.5(4)
C32	0.0552(5)	0.1345(3)	0.0382(4)	2.9(4)
C33	0.0016(5)	0.1281(4)	-0.0369(4)	3.7(4)
C34	0.0087(5)	0.0756(4)	-0.0779(4)	3.5(4)
C35	-0.0509(6)	0.0706(4)	-0.1591(4)	5.0(5)
C36	0.0717(5)	0.0288(4)	-0.0420(4)	3.2(4)
C37	0.1262(5)	0.0328(3)	0.0327(4)	3.1(4)
C38	0.1196(4)	0.0861(3)	0.0747(4)	2.7(4)
C39	0.1991(5)	-0.0172(4)	0.0667(4)	3.3(4)
C40	0.3089(5)	-0.0026(4)	0.0051(4)	4.0(4)
C41	0.3765(5)	0.0424(4)	0.0129(4)	3.9(5)
C42	0.4290(6)	0.0569(5)	-0.0287(5)	5.2(5)
C43	0.4902(6)	0.1055(5)	-0.0042(5)	5.9(6)
C44	0.5020(6)	0.1411(5)	0.0597(5)	6.0(6)
C45	0.4525(5)	0.1277(4)	0.1017(4)	4.8(5)
C46	0.3881(5)	0.0782(4)	0.0771(4)	3.7(4)
C47	0.1787(8)	0.2732(6)	0.2749(7)	10.5(9)
C48	0.2993(12)	0.2829(9)	0.3863(11)	23.5(17)
C49	0.1985(10)	0.3687(7)	0.3536(11)	17.4(15)
C50	0.2796(7)	0.2174(5)	0.1186(6)	7.6(7)
C51	0.2205(13)	0.3085(11)	0.0363(14)	28.1(24)
C52	0.3587(22)	0.3077(9)	0.1389(12)	34.9(35)
C11	0.34151(18)	0.78700(14)	0.07625(16)	7.47(18)
O5	0.3156(7)	0.8497(4)	0.0588(5)	13.6(8)
O6	0.2725(7)	0.7533(7)	0.0825(7)	20.9(11)
O7	0.3598(7)	0.7600(4)	0.0179(5)	14.0(8)
O8	0.4163(6)	0.7840(5)	0.1410(5)	14.0(7)
C12	0.9984(3)	0.38899(18)	0.12552(20)	13.3(3)
O9	0.9932(11)	0.3306(5)	0.1204(8)	25.8(15)
O10	0.870(3)	0.4043(8)	0.0376(12)	63.6(48)
O11	0.9932(9)	0.4201(5)	0.1785(5)	17.8(10)
O12	1.0693(14)	0.4021(11)	0.1134(11)	37.7(26)
O13	0.2875(4)	0.9405(3)	0.2482(4)	7.8(4)
N11	0.3029(6)	0.8377(4)	0.2913(4)	7.7(5)
C53	0.3115(7)	0.8851(5)	0.2499(5)	7.1(6)
C54	0.3356(11)	0.7740(6)	0.2898(8)	13.4(12)
C55	0.2628(10)	0.8467(7)	0.3428(7)	12.6(11)

*Beq is the Mean of the Principal Axes of the Thermal Ellipsoid

Table 2. Selected Bond Distances/Å Angles/deg of the Complex 2

Bond Distance/Å			
Cu(1)···Cu(2)	3.094(1)	Cu(1)-N(1)	1.981(6)
Cu(1)-N(5)	1.999(6)	Cu(1)-O(1)	1.953(5)
Cu(1)-O(2)	1.980(4)	Cu(1)-O(3)	2.348(6)
Cu(2)-N(4)	1.975(6)	Cu(2)-N(7)	1.992(6)
Cu(2)-O(1)	1.963(5)	Cu(2)-O(2)	1.971(5)
Cu(2)-O(4)	2.372(6)		
Bond Angle/deg			
Cu(1)-O(1)-Cu(2)	104.39(21)	Cu(1)-O(2)-Cu(2)	103.10(20)
N(1)-Cu(1)-O(1)	97.99(23)	N(1)-Cu(1)-O(2)	167.83(24)
N(1)-Cu(1)-O(3)	88.8(3)	N(5)-Cu(1)-O(1)	168.79(22)
N(5)-Cu(1)-O(2)	93.90(21)	N(5)-Cu(1)-O(3)	100.96(25)
O(1)-Cu(1)-O(2)	75.98(19)	O(1)-Cu(1)-O(3)	85.94(23)
O(2)-Cu(1)-O(3)	101.16(22)	O(1)-Cu(2)-O(2)	75.95(18)
O(1)-Cu(2)-O(4)	99.33(21)	O(2)-Cu(2)-O(4)	89.66(20)
N(1)-Cu(1)-N(5)	91.03(24)	N(4)-Cu(2)-N(7)	90.79(24)
N(4)-Cu(2)-O(1)	96.72(22)	N(4)-Cu(2)-O(2)	172.63(21)
N(4)-Cu(2)-O(4)	92.39(23)	N(7)-Cu(2)-O(1)	169.72(22)
N(7)-Cu(2)-O(2)	96.38(21)	N(7)-Cu(2)-O(4)	87.32(23)

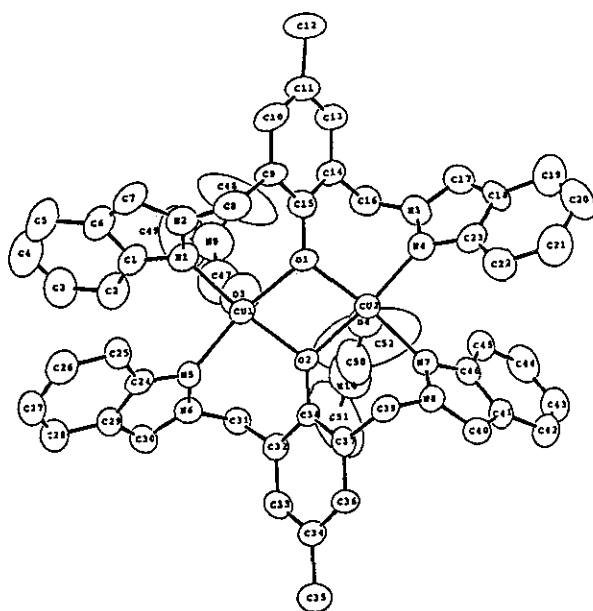


Fig. 1. Molecular structure of complex 2.

that of complex $[\text{Cu}_2(\text{bpeac})(\text{AcO})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ (bpeacH = 2,6-bis(bis(2-(1-pyrazolyl)ethyl)amino)-*p*-cresol)¹⁵. The phenolate oxygen bridge angles Cu(1)-O(1)-Cu(2) and Cu(1)-O(2)-Cu(2) are 104.39(21) and 103.10(20)°, respectively. The Cu-O (oxygen atom from DMF) distances, 2.348(6) and 2.372(6) Å are markedly longer than the Cu-O (oxygen atom from phenolate) distances, 1.953(5), 1.980(4), 1.963(5) and 1.971(5) Å. There are one DMF molecule as solvent and two perchlorate counter anions in the complex 2.

The UV/visible spectrum for the complex 2 exhibits a strong line due to charge transfer from phenolate to copper(II) at 434 nm ($\epsilon = 5380 \text{ M}^{-1}\text{cm}^{-1}$) and a much weaker d-d line ($\lambda_{\text{max}} = 680 \text{ nm}$, $\epsilon = 790 \text{ M}^{-1}\text{cm}^{-1}$). The powder EPR spectrum and magnetic moment were measured at room temperature. There was no EPR signal, and the magnetic moment of the complex is a small value 1.17 per copper. These properties indicate a strong antiferromagnetic coupling between the two copper(II) ions.¹⁶

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Key Words

Dicopper complex; Indazole; Antiferromagnetic effect.

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