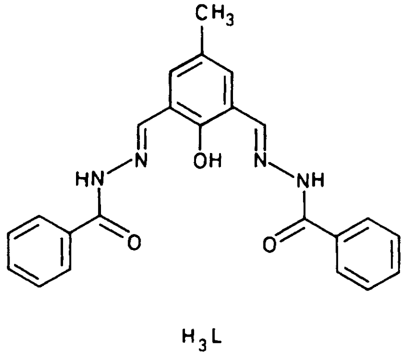
Crystal Structures and Magnetic Properties of Bi- and Tetra-nuclear Copper(II) Complexes of 2,6-Diformyl-4-methylphenol Di(benzoylhydrazone)†

Masatomi Sakamoto,* Shoichi Itose, and Tomitaro Ishimori
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790, Japan
Naohide Matsumoto,* Hisashi Ōkawa, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan

The crystal structures of the bi- and the tetra-nuclear copper(II) complexes $[Cu_2L(OCH_3)]\cdot dmf$ (**1**) and $[\{Cu_2L(OH)\cdot dmf\}_2]$ (**2**) have been determined, where H_3L denotes 2,6-diformyl-4-methylphenol di(benzoylhydrazone). Complex (**1**) assumes a binuclear structure, in which two copper(II) ions are bridged by an endogenous phenolic oxygen atom of the dinucleating ligand L and an exogenous methoxide oxygen atom. Two molecules are stacked parallel in the crystal, where the shortest intermolecular Cu ··· Cu and Cu ··· O distances are 3.572(1) and 3.645(5) Å, respectively. Complex (**2**) assumes a tetranuclear structure composed of two binuclear units related by a centre of symmetry. Two copper(II) ions in the crystallographically unique binuclear unit are bridged by the endogenous phenolic oxygen atom and an exogenous hydroxide oxygen atom. The hydroxide oxygen further co-ordinates to an axial position of a copper(II) ion of an adjacent binuclear unit related by the centre of symmetry with a bond distance of 2.322(5) Å. Cryomagnetic data for complexes (**1**) and (**2**) (80—300 K) can be reproduced by an equation based on the Heisenberg model ($H = -2JS_1S_2$, $S_1 = S_2 = \frac{1}{2}$) with the parameters of $J = -315$ cm^{-1} and $g = 2.05$ for (**1**) and $J = -190$ cm^{-1} and $g = 2.10$ for (**2**), although in the case of (**2**) the interdimer distances of Cu(2) ··· Cu(2^{II}) ($1 - x, -y, 2 - z$) and Cu(1) ··· Cu(2^{II}) are only 3.186(1) and 3.282(1) Å respectively. The magnetism of complex (**2**) implies that the intradimer antiferromagnetic interaction through the endogenous phenolic oxygen is predominant, and the intra- and inter-dimer magnetic interactions through the exogenous hydroxide oxygen atom contribute little to the magnetic susceptibility, because the hydroxide oxygen atom is bound to four atoms (3Cu and H) and hence has no lone-pair electrons.

The magnetic spin exchange in binuclear copper(II) complexes in respect of stereochemical factors and the nature of the bridging groups is of continuing interest.[1] The design of ligands capable of binding two metal ions in close proximity is, therefore, an important subject in this field. The di-Schiff bases of 2,6-diformyl-4-methylphenol were first developed by Robson[2] and our group.[3] A related dithiosemicarbazone was used by Hoskins *et al.*[4] for the synthesis of binuclear copper(II) and nickel(II) complexes. This type of ligand is known to form binuclear complexes bridged by two different groups, *i.e.* the endogenous phenolic oxygen and an exogenous groups such as hydroxide, alkoxide, halide, pseudohalide, carboxylate, or pyrazolate ion. Later it was extensively used for the study of spin-exchange interaction and for modelling of the active site of type III copper proteins.[5—7]

In order to gain an insight into the correlation between the structure and magnetism of binuclear copper(II) complexes, detailed investigations based on crystal structure analyses are needed. *X*-Ray structural evidence for the copper(II) complexes of this group is very limited.[7] In this study we have obtained bi- and tetra-nuclear copper(II) complexes of 2,6-diformyl-4-methylphenol di(benzoylhydrazone) (H_3L, see drawing), $[Cu_2L(OCH_3)]\cdot dmf$ (**1**) and $[\{Cu_2L(OH)\cdot dmf\}_2]$ (**2**) (dmf = dimethylformamide). Their single-crystal *X*-ray analyses and cryomagnetic properties are described.



H_3L

Experimental

Synthesis.—2,6-Diformyl-4-methylphenol was synthesized according to the method of Ōkawa and Kida[8a] which is a modification of a previous method.[8b] Benzohydrazide was purchased from Aldrich Chem. Co.

Dinucleating ligand H_3L. To an ethanolic solution (35 cm^3) of 2,6-diformyl-4-methylphenol (1 mmol) was added benzohydrazide (2 mmol) in ethanol (10 cm^3). To this solution was added one drop of concentrated HCl and the mixture was heated at *ca.* 60 °C for 1 h and allowed to stand overnight. The precipitate was filtered off, washed with ethanol, and dried in air. Yield *ca.* 80%.

$[Cu_2L(OCH_3)]\cdot dmf$ (**1**). An aqueous solution (10 cm^3) of

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. ≈ 9.27×10^{-24} J T^{-1}.

Table 1. Positional parameters (× 10^4) of non-hydrogen atoms of complex (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	844(1)	2 144(0)	4 285(1)	C(11)	2 691(6)	−512(4)	372(9)
Cu(2)	−924(1)	467(0)	3 481(1)	C(12)	3 465(7)	−1 005(5)	−563(11)
O(1)	592(4)	881(3)	3 088(6)	C(13)	1 630(6)	−942(4)	551(9)
O(2)	−657(4)	1 718(3)	4 595(7)	C(14)	909(5)	−501(4)	1 462(8)
O(3)	1 244(4)	3 392(3)	5 486(7)	C(15)	1 257(5)	443(4)	2 236(8)
O(4)	−2 407(4)	−56(3)	3 770(6)	C(16)	−175(6)	−1 045(4)	1 562(9)
N(1)	2 884(5)	3 296(3)	4 345(8)	C(17)	−2 627(6)	−915(4)	3 069(9)
N(2)	2 311(5)	2 394(3)	3 690(7)	C(18)	−3 768(6)	−1 449(4)	3 092(9)
N(3)	−927(5)	−743(3)	2 353(7)	C(19)	−4 112(7)	−2 366(5)	2 248(11)
N(4)	−1 924(5)	−1 358(3)	2 326(8)	C(20)	−5 166(8)	−2 846(5)	2 336(13)
C(1)	2 002(7)	5 258(5)	6 607(11)	C(21)	−5 879(7)	−2 444(5)	3 242(13)
C(2)	2 431(9)	6 182(5)	7 294(13)	C(22)	−5 550(7)	−1 543(5)	4 092(13)
C(3)	3 565(9)	6 527(5)	7 435(13)	C(23)	−4 496(6)	−1 045(5)	4 009(11)
C(4)	4 296(8)	5 993(5)	6 917(15)	CM	−1 329(7)	2 204(5)	5 580(11)
C(5)	3 870(7)	5 073(5)	6 252(12)	CD(1)	1 711(16)	5 261(7)	1 722(18)
C(6)	2 721(6)	4 710(4)	6 057(9)	CD(2)	2 153(15)	3 815(11)	203(19)
C(7)	2 244(6)	3 730(4)	5 259(9)	ND	1 500(7)	4 327(5)	1 087(10)
C(8)	2 806(6)	1 858(4)	2 791(9)	CD	502(11)	3 867(8)	1 469(18)
C(9)	2 342(5)	897(4)	2 059(8)	OD	156(7)	3 079(5)	950(13)
C(10)	3 019(6)	407(4)	1 134(9)				

Table 2. Positional parameters (× 10^4) of non-hydrogen atoms of complex (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	4 520(1)	846(1)	7 598(1)	C(10)	3 024(7)	−2 116(7)	3 225(8)
Cu(2)	5 810(1)	−767(1)	9 037(1)	C(11)	3 300(7)	−3 195(6)	3 121(8)
O(1)	4 725(5)	−703(4)	7 105(5)	C(12)	2 731(10)	−4 105(7)	1 692(10)
O(2)	5 553(4)	784(4)	9 532(5)	C(13)	4 095(7)	−3 400(6)	4 372(9)
O(3)	4 305(5)	2 361(4)	7 827(6)	C(14)	4 616(7)	−2 582(6)	5 723(8)
O(4)	7 099(5)	−932(4)	10 728(6)	C(15)	4 281(7)	−1 499(6)	5 837(8)
N(1)	3 114(6)	1 697(5)	5 334(7)	C(16)	5 502(7)	−2 910(6)	6 890(8)
N(2)	3 506(5)	711(5)	5 583(7)	C(17)	7 436(7)	−1 937(6)	10 406(9)
N(3)	6 070(6)	−2 270(5)	8 181(7)	C(18)	8 418(7)	−2 227(6)	11 555(9)
N(4)	6 969(6)	−2 699(5)	9 142(7)	C(19)	8 727(8)	−3 296(6)	11 411(10)
C(1)	3 775(8)	4 487(6)	7 860(9)	C(20)	9 648(8)	−3 554(8)	12 499(11)
C(2)	3 479(9)	5 537(7)	7 866(10)	C(21)	10 299(8)	−2 733(8)	13 733(12)
C(3)	2 690(9)	5 742(7)	6 625(12)	C(22)	10 008(9)	−1 670(8)	13 870(11)
C(4)	2 215(9)	4 889(8)	5 334(12)	C(23)	9 059(8)	−1 427(6)	12 800(10)
C(5)	2 511(8)	3 851(6)	5 308(10)	C1(D)	71(10)	7 049(8)	8 325(14)
C(6)	3 285(7)	3 631(6)	6 580(9)	C2(D)	−649(10)	8 814(9)	7 941(13)
C(7)	3 593(7)	2 492(6)	6 590(9)	C3(D)	1 455(8)	8 558(7)	8 908(11)
C(8)	3 160(7)	−173(6)	4 484(9)	N(D)	358(7)	8 165(6)	8 405(9)
C(9)	3 495(7)	−1 263(6)	4 549(8)	O(D)	2 312(6)	8 040(5)	9 350(8)

copper(II) acetate monohydrate (2.2 mmol) was added to a methanolic solution (40 cm^3) of H_3L (1 mmol). The solution was allowed to stand for several hours at room temperature. The crude complex precipitated was collected by suction filtration and dried. Yield 90% (Found: C, 51.90; H, 3.75; Cu, 22.60; N, 10.20. Calc. for $C_{24}H_{19}Cu_2N_4O_4$: C, 51.90; H, 3.65; Cu, 22.90; N, 10.10%). The complex was recrystallized from hot methanol–dimethylformamide (1:1, v/v) to give dark green crystals of formula $[Cu_2L(OCH_3)]$·dmf (**1**). Yield *ca.* 30% (Found: C, 51.95; H, 4.35; Cu, 20.15; N, 11.15. Calc. for $C_{27}H_{27}Cu_2N_5O_5$: C, 51.60; H, 4.35; Cu, 20.20; N, 11.15%).

$[\{Cu_2L(OH)·dmf\}_2]$ (**2**). The crude complex was recrystallized from a hot dimethylformamide solution to give dark green crystals of (**2**). Yield *ca.* 30% (Found: C, 50.75; H, 4.10; Cu, 20.65; N, 11.35. Calc. for $C_{26}H_{24}Cu_2N_5O_5$: C, 50.80; H, 4.10; Cu, 20.70; N, 11.40%).

Physical Measurements.—Elemental analyses were carried out at the Analysis Center of Kyushu University and Advanced Instrumentation Center for Chemical Analysis, Ehime. Thermogravimetric analyses were carried out on a Cahn 2000 recording electrobalance with a heating rate of 5° min^{-1} in a stream of nitrogen. Infrared spectra were recorded on a JASCO IR-G spectrophotometer, reflectance spectra on a Shimadzu MPS-5000 spectrophotometer. Magnetic susceptibilities were determined by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). The susceptibility data were corrected for the magnetization of the sample holder and for the diamagnetism of the component atoms by the use of Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{eff.} = 2.828\sqrt{\chi_A T}$.

X-Ray Diffraction Analyses.—Crystals suitable for *X*-ray analysis were obtained from a solution of dimethylformamide–methanol (1:1, v/v) for complex (**1**) and hot dimethylformamide for (**2**), respectively. Crystallographic data were collected on a Rigaku Denki AFC-5 four-circle automated *X*-ray diffractometer, using graphite-monochromatized Mo-K_α radiation at room temperature. The data were corrected for Lorentz and polarization effects. No absorption corrections were made. All computations were carried out with a locally modified version of the UNICS III program system[9] on a FACOM M 780 computer at the Computer Center of Kyushu University.

Crystal data for $[Cu_2L(OCH_3)]$·dmf (**1**). $C_{27}H_{27}Cu_2N_5O_5$,

M = 628.6, triclinic, space group $P\bar{1}$, a = 12.035(2), b = 15.461(3), c = 7.614(1) Å, α = 101.03(1), β = 101.06(1), γ = 99.55(1)°, U = 1 334.2 Å^3, D_c = 1.565 g cm^{-3} (Z = 2), λ(Mo-K_α) = 0.710 69 Å, F(000) = 644, μ(Mo-K_α) = 16.43 cm^{-1}, crystal size 0.2 × 0.2 × 0.3 mm, scan mode θ—2θ, scan speed 6° min^{-1}, scan width (1.1 + 0.35 tan θ°), 2θ range 2.5—52°, octant measured $+h$, $\pm k$, $\pm l$, observed reflections with $|F_o| > 3\sigma(|F_o|)$ 3 952, R = 0.046, R' = 0.065, highest peak in the final difference Fourier map 1.0 e Å^{-3} (around dmf molecule).

Crystal data for [{Cu$_2$L(OH)·dmf}$_2$] (**2**). $C_{26}H_{24}Cu_2N_5O_5$, M = 613.6, triclinic, space group $P\bar{1}$, a = 11.653(2), b = 12.765(2), c = 9.318(2) Å, α = 106.23(1), β = 104.68(1), γ = 88.32(1)°, U = 1 286.1(4) Å^3, D_c = 1.585 g cm $^{-3}$ (Z = 2), λ(Mo-K_α) = 0.710 69 Å, F(000) = 626, μ(Mo-K_α) = 17.02 cm^{-1}, crystal size 0.4 × 0.2 × 0.3 mm, scan mode and speed as above, scan width (1.0 + 0.35 tan θ°), 2θ range 2.5—45°, octant measured $+h$, $\pm k$, $\pm l$, observed reflections with $|F_o| > 3\sigma(|F_o|)$ 2 873, R = 0.052, R' = 0.058, highest peak in the final difference Fourier map 0.5 e Å^{-3}.

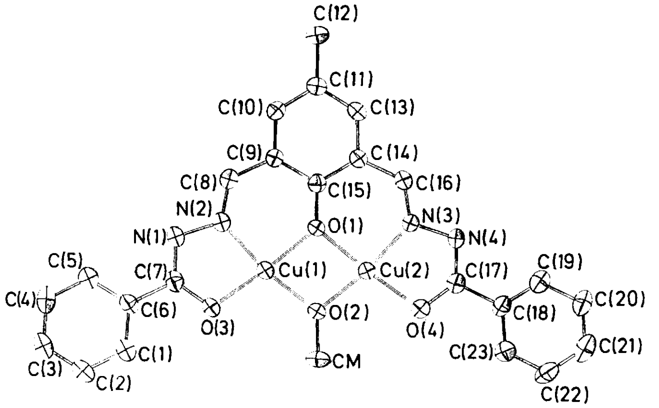


Figure 1. ORTEP drawing of complex (**1**) with the atom numbering scheme

Structures were solved by the heavy-atom method. In all refinements, the function minimized was $\Sigma w(|F_o| - |F_c|)$ and atomic scattering factors were taken from ref. 10. Hydrogen atoms were included in the molecular model in geometrically idealized positions. The final refinement was carried out by block-diagonal least squares with isotropic thermal parameters for the H atoms and anisotropic parameters for the non-hydrogen atoms, where equal weight w = 1 was adopted. Positional parameters of non-hydrogen atoms of complexes (**1**) and (**2**) are listed in Tables 1 and 2, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The i.r. spectrum of the free ligand H$_3$L shows a sharp ν(OH) band of phenol and ν(NH) of hydrazone at 3 400 and 3 175 cm^{-1}, respectively. These bands disappear on formation of complex (**1**). For complex (**2**), the ν(OH) absorption of exogenous bridging hydroxide ion is observed at 3 400 cm^{-1}, but the ν(NH) band is absent. Thermogravimetric analyses of (**1**) and (**2**) showed a weight loss corresponding to the elimination of one dmf molecule per binuclear unit in the temperature range 100—180 °C. The reflectance spectrum showed a broad absorption at 625 nm assignable to *d*—*d* transitions and absorption at 440 nm assignable to a charge-transfer transition.

Structural Description of Complex (**1**).—The ORTEP drawing of [Cu$_2$L(OCH$_3$)] with the atom numbering scheme is shown in Figure 1. Bond distances and angles with their

Table 3. Bond distances (Å) and angles (°) of [Cu$_2$L(OCH$_3$)]·dmf (**1**)*

Cu(1)–Cu(2)	2.947(1)	Cu(2) ··· Cu(2^{I})	3.572(1)	C(10)–C(11)	1.386(10)	C(11)–C(12)	1.496(11)
Cu(1)–O(1)	1.937(5)	Cu(1)–O(2)	1.892(5)	C(11)–C(13)	1.383(10)	C(13)–C(14)	1.395(10)
Cu(1)–O(3)	1.907(5)	Cu(1)–N(2)	1.902(6)	C(14)–C(15)	1.424(9)	C(14)–C(16)	1.454(10)
Cu(2)–O(1)	1.930(5)	Cu(2)–O(2)	1.904(5)	N(3)–C(16)	1.282(9)	N(3)–N(4)	1.396(8)
Cu(2)–O(4)	1.905(5)	Cu(2)–N(3)	1.902(6)	N(4)–C(17)	1.317(9)	O(4)–C(17)	1.295(8)
O(1)–C(15)	1.314(8)	O(2)–CM	1.414(10)	C(17)–C(18)	1.486(10)	C(18)–C(19)	1.396(11)
O(3)–C(17)	1.288(9)	N(1)–N(2)	1.397(8)	C(19)–C(20)	1.380(13)	C(20)–C(21)	1.357(14)
N(1)–C(7)	1.314(9)	C(6)–C(7)	1.490(11)	C(21)–C(22)	1.374(14)	C(22)–C(23)	1.390(13)
C(1)–C(6)	1.375(12)	C(1)–C(2)	1.395(14)	C(18)–C(23)	1.376(11)		
C(2)–C(3)	1.356(15)	C(3)–C(4)	1.364(15)	ND–CD(1)	1.396(21)	ND–CD(2)	1.379(21)
C(4)–C(5)	1.389(14)	C(5)–C(6)	1.371(12)	ND–CD	1.401(17)	CD–OD	1.182(17)
N(2)–C(8)	1.271(9)	C(8)–C(9)	1.455(10)				
C(9)–C(10)	1.397(9)	C(9)–C(15)	1.420(9)				
Cu(1)–O(1)–Cu(2)	99.3(2)	Cu(1)–O(1)–C(15)	130.0(4)	C(9)–C(10)–C(11)	123.4(6)	C(10)–C(11)–C(12)	121.0(6)
Cu(2)–O(1)–C(15)	130.7(4)	Cu(1)–O(2)–Cu(2)	101.8(2)	C(10)–C(11)–C(13)	116.5(6)	C(12)–C(11)–C(13)	122.3(6)
Cu(1)–O(2)–CM	127.7(5)	Cu(2)–O(2)–CM	130.1(5)	C(11)–C(13)–C(14)	123.3(6)	C(13)–C(14)–C(15)	119.4(6)
O(1)–Cu(1)–O(2)	79.4(2)	O(2)–Cu(1)–O(3)	105.6(2)	C(13)–C(14)–C(16)	117.1(6)	C(15)–C(14)–C(16)	123.4(6)
O(3)–Cu(1)–N(2)	83.4(2)	O(1)–Cu(1)–N(2)	91.6(2)	C(14)–C(15)–O(1)	120.9(6)	C(14)–C(15)–C(9)	117.9(6)
O(1)–Cu(2)–O(2)	79.4(2)	O(2)–Cu(2)–O(4)	106.1(2)	C(9)–C(15)–O(1)	121.1(6)	C(14)–C(16)–N(3)	124.7(6)
O(4)–Cu(2)–N(3)	83.2(2)	O(1)–Cu(2)–N(3)	91.2(2)	C(16)–N(3)–N(4)	117.5(5)	Cu(2)–N(3)–C(16)	128.7(5)
Cu(1)–O(3)–C(7)	108.5(4)	O(3)–C(7)–N(1)	126.1(6)	Cu(2)–N(3)–N(4)	113.7(4)	N(3)–N(4)–C(17)	108.6(5)
O(3)–C(7)–C(6)	117.8(6)	N(1)–C(7)–C(6)	116.0(6)	N(4)–C(17)–O(4)	125.4(6)	N(4)–C(17)–C(18)	116.9(6)
C(7)–C(6)–C(1)	119.6(7)	C(7)–C(6)–C(5)	120.8(7)	O(4)–C(17)–C(18)	117.6(6)	Cu(2)–O(4)–C(17)	109.0(4)
C(1)–C(6)–C(5)	119.5(8)	C(6)–C(1)–C(2)	120.0(8)	C(17)–C(18)–C(19)	121.5(6)	C(17)–C(18)–C(23)	119.8(6)
C(1)–C(2)–C(3)	119.3(9)	C(2)–C(3)–C(4)	121.5(10)	C(19)–C(18)–C(23)	118.6(7)	C(18)–C(19)–C(20)	119.9(8)
C(3)–C(4)–C(5)	119.0(10)	C(4)–C(5)–C(6)	120.4(8)	C(19)–C(20)–C(21)	121.1(9)	C(20)–C(21)–C(22)	119.7(9)
C(7)–N(1)–N(2)	108.6(5)	Cu(1)–N(2)–N(1)	113.4(4)	C(21)–C(22)–C(23)	120.1(9)	C(22)–C(23)–C(18)	120.4(8)
Cu(1)–N(2)–C(8)	128.6(5)	N(1)–N(2)–C(8)	118.0(5)				
N(2)–C(8)–C(9)	124.9(6)	C(8)–C(9)–C(10)	117.0(6)	CD(1)–ND–CD(2)	128.7(13)	CD(1)–ND–CD	113.8(11)
C(8)–C(9)–C(15)	123.7(6)	C(10)–C(9)–C(15)	119.2(6)	CD(2)–ND–CD	117.3(11)	ND–CD–OD	123.1(12)

* Symmetry equivalent position: I $-x$, $-y$, $1 - z$.

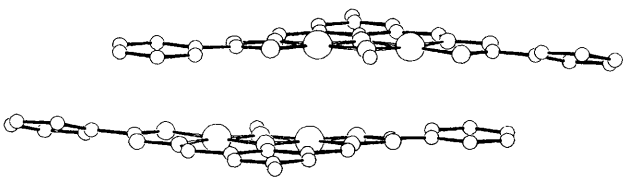


Figure 2. Stacking view of two molecules of complex (**1**)

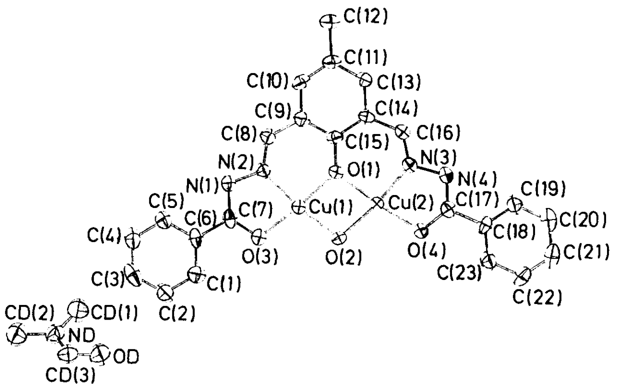


Figure 3. Crystallographically unique molecule of (**2**) with the atom numbering scheme

estimated standard deviations are given in Table 3. The stacking of the molecules in the crystal is shown in Figure 2. Two molecules are stacked parallel, where the shortest intermolecular Cu ··· Cu and Cu ··· O distances are 3.572(1) Å of Cu(2) ··· Cu(2$^{\text{I}}$) (−*x*, −*y*, 1 − *z*) and 3.645(5) Å of Cu(2) ··· O(1$^{\text{I}}$), respectively. Complex (**1**) can be described as binuclear, the two copper(II) ions being bridged by an endogenous phenolic oxygen atom O(1) and an exogenous methoxide oxygen atom O(2). The co-ordination geometries of Cu(1) and Cu(2) are similar and are best described as square planar, since the shortest Cu–O (axial position) distance is 3.645(5) Å of Cu(2) ··· O(1$^{\text{I}}$), The co-ordination bond distances of Cu(1) agree well with the corresponding bond distances of Cu(2) within their experimental errors. The deviations of Cu(1) and Cu(2) from their co-ordination planes are less than 0.03 Å.

Structural Description of Complex (**2**).—The crystallographically unique molecule with the atom numbering scheme is shown in Figure 3, the atom numbering system being as that for complex (**1**). Bond distances and angles with their estimated standard deviations are listed in Table 4. Atoms Cu(1) and Cu(2) of the crystallographically unique unit are bridged by an endogenous phenolic oxygen atom O(1) and an exogenous hydroxide oxygen atom O(2). Two binuclear units related by the centre of symmetry are bridged by two hydroxide oxygen atoms O(2) and O(2$^{\text{II}}$) (1 − *x*, −*y*, 2 − *z*) with the bond distance Cu(2)–O(2$^{\text{II}}$) 2.322(5) Å, and as a result form a tetranuclear structure in a stepped geometry (Figure 4). The co-ordination geometries of Cu(1) and Cu(2) in the crystallographically unique unit are different. That of Cu(1) is best described as square planar, while the oxygen atom of hydrazone O(4$^{\text{II}}$) of the adjacent binuclear unit approaches Cu(1) with a long distance of Cu(1)–O(4$^{\text{II}}$) 2.718(6) Å. The co-ordination geometry of Cu(2) is square pyramidal, the equatorial co-ordination plane being formed by O(1), O(2), O(4), and N(3) of the binuclear unit, and the axial co-ordination site being occupied by O(2$^{\text{II}}$) of the adjacent binuclear unit [Cu(2)–O(2$^{\text{II}}$) 2.322(5) Å]. Atom Cu(2) deviates by 0.14 Å toward the axial ligand O(2$^{\text{II}}$) from the equatorial co-ordination plane. Due to the difference in co-ordination geometries around Cu(1) and Cu(2), the bond distances of Cu(1) are shorter than the corresponding ones of Cu(2). For example, Cu(1)–O(1) [1.922(4) Å] is shorter than Cu(2)–O(1) [1.941(4) Å].

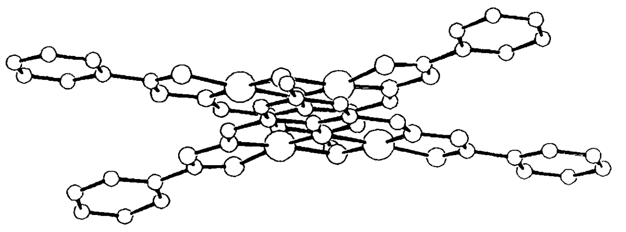


Figure 4. Edge-on view of the tetranuclear structure of complex (**2**)

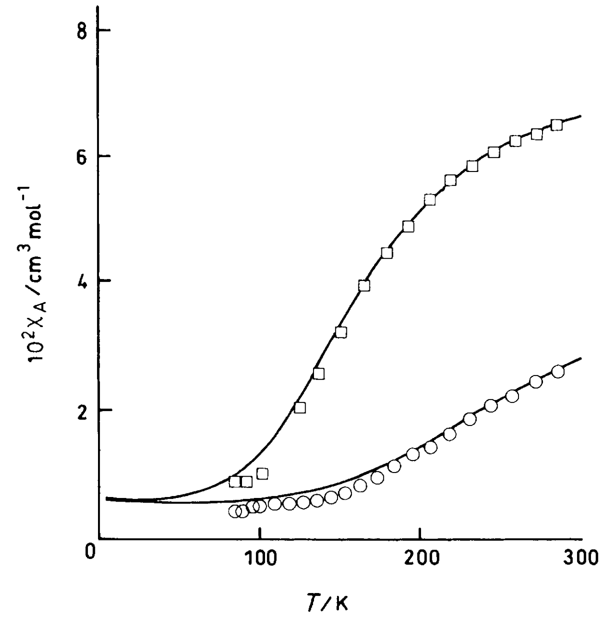


Figure 5. Temperature dependences of the magnetic susceptibilities of complex (**1**) (○) and (**2**) (□), where the solid lines represent the theoretical curves drawn with the parameters $J = -315$ cm^{-1}, $g = 2.05$, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} for (**1**) and $J = -190$ cm^{-1}, $g = 2.10$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} for (**2**)

Structural Parameters Related to the Magnetic Properties.—*Complex* (**1**). The Cu–O–Cu angles of the Cu_2O_2 core consisting of Cu(1), Cu(2), O(1), and O(2) are 99.3(2) (phenolic) and 101.8(2)° (methoxide). The co-ordination planes of Cu(1) and Cu(2) are coplanar, the maximum deviation from the plane defined by Cu(1), Cu(2), O(1), O(2), O(3), O(4), N(1), N(2), N(3), and N(4) being 0.09 Å. The sums of the bond angles around the phenolic [O(1)] and methoxide [O(2)] oxygen atoms are 359.6 and 360.0°, respectively.

Complex (**2**). The Cu–O–Cu angles in the intradimer Cu_2O_2 core consisting of Cu(1), Cu(2), O(1), and O(2) are 99.0(1) (phenolic) and 99.4(1)° (hydroxide). The corresponding angle of the interdimer Cu_2O_2 core consisting of Cu(2), Cu(2$^{\text{II}}$), O(2), and O(2$^{\text{II}}$) is 96.4(2)°. The dihedral angle between two co-ordination planes in the binuclear unit is 9.1°. The planarity of bonds to the bridging oxygens can be estimated by the sum of the bond angles around the bridging oxygen: that for the phenolic oxygen O(1) is 359.9°, while that for the hydroxide oxygen O(2) is 296.8°.

Magnetic Properties.—The temperature dependences of the magnetic susceptibilities per copper atom of complexes (**1**) and (**2**) are shown in Figure 5.

Complex (**1**). The magnetic moment at room temperature (247.8 K) is 0.81 B.M., much smaller than the spin-only value

Table 4. Bond distances (Å) and angles (°) of $[\{Cu_2L(OH)\cdot dmf\}_2]$ (**2**) *

Cu(1)–Cu(2)	2.938(1)	Cu(1) · · · Cu(2$^{\mathrm{II}}$)	3.282(1)	C(9)–C(15)	1.414(10)	C(10)–C(11)	1.387(11)
Cu(2) · · · Cu(2$^{\mathrm{II}}$)	3.186(1)	Cu(1)–O(1)	1.922(4)	C(11)–C(12)	1.514(9)	C(11)–C(13)	1.376(10)
Cu(1)–O(2)	1.917(4)	Cu(1)–O(3)	1.901(5)	C(13)–C(14)	1.399(8)	C(14)–C(15)	1.406(10)
Cu(1)–N(2)	1.912(5)	Cu(1)–O(4$^{\mathrm{II}}$)	2.718(6)	O(1)–C(15)	1.321(7)	C(14)–C(16)	1.444(10)
Cu(2)–O(1)	1.941(4)	Cu(2)–O(2)	1.935(4)	N(3)–C(16)	1.276(7)	C(17)–C(18)	1.472(10)
Cu(2)–O(4)	1.936(4)	Cu(2)–N(3)	1.909(5)	C(18)–C(19)	1.378(11)	C(18)–C(23)	1.375(9)
Cu(2)–O(2$^{\mathrm{II}}$)	2.322(5)	O(3)–C(7)	1.288(9)	C(19)–C(20)	1.380(12)	C(20)–C(21)	1.388(11)
N(1)–C(7)	1.323(8)	N(1)–N(2)	1.386(8)	C(21)–C(22)	1.367(14)	C(22)–C(23)	1.381(12)
O(4)–C(17)	1.305(8)	N(4)–C(17)	1.302(8)				
N(3)–N(4)	1.400(8)	N(2)–C(8)	1.286(8)	CD(1)–ND	1.450(13)	CD(2)–ND	1.461(13)
C(8)–C(9)	1.447(11)	C(9)–C(10)	1.396(9)	ND–CD(3)	1.306(11)	CD(3)–OD	1.228(11)
Cu(1)–O(1)–Cu(2)	99.0(1)	Cu(1)–O(2)–Cu(2)	99.4(1)	N(4)–N(3)–C(16)	118.3(5)	N(3)–C(16)–C(14)	125.1(6)
Cu(1)–O(2)–Cu(2$^{\mathrm{II}}$)	101.0(2)	Cu(2)–O(2)–Cu(2$^{\mathrm{II}}$)	96.4(2)	C(8)–C(9)–C(10)	116.6(6)	C(8)–C(9)–C(15)	124.1(5)
Cu(1)–O(4$^{\mathrm{II}}$)–Cu(2$^{\mathrm{II}}$)	88.0(2)	O(1)–Cu(1)–O(2)	81.2(1)	C(10)–C(9)–C(15)	119.2(6)	C(9)–C(10)–C(11)	122.3(7)
O(2)–Cu(1)–O(3)	104.6(1)	O(3)–Cu(1)–N(2)	82.6(2)	C(10)–C(11)–C(12)	120.9(7)	C(10)–C(11)–C(13)	117.2(6)
N(2)–Cu(1)–O(1)	91.4(2)	O(4$^{\mathrm{II}}$)–Cu(1)–O(1)	97.8(2)	C(12)–C(11)–C(13)	121.8(7)	C(11)–C(13)–C(14)	123.2(6)
O(4$^{\mathrm{II}}$)–Cu(1)–O(2)	80.0(1)	O(4$^{\mathrm{II}}$)–Cu(1)–O(3)	91.8(2)	C(13)–C(14)–C(15)	118.6(6)	C(13)–C(14)–C(16)	116.9(6)
O(4$^{\mathrm{II}}$)–Cu(1)–N(2)	101.1(2)	O(2$^{\mathrm{II}}$)–Cu(2)–O(1)	99.3(2)	C(15)–C(14)–C(16)	124.3(5)	C(14)–C(15)–C(9)	119.0(5)
O(2$^{\mathrm{II}}$)–Cu(2)–O(2)	83.5(2)	O(2$^{\mathrm{II}}$)–Cu(2)–O(4)	90.7(2)	O(1)–C(15)–C(9)	120.0(6)	O(1)–C(15)–C(14)	120.9(6)
O(2$^{\mathrm{II}}$)–Cu(2)–N(3)	104.7(2)	Cu(1)–O(1)–C(15)	131.3(4)	C(7)–C(6)–C(11)	119.5(7)	C(7)–C(6)–C(5)	121.3(6)
Cu(2)–O(1)–C(15)	129.6(4)	O(1)–Cu(2)–O(2)	80.3(1)	C(1)–C(6)–C(5)	119.1(7)	C(6)–C(1)–C(2)	119.7(7)
O(2)–Cu(2)–O(4)	104.7(1)	O(4)–Cu(2)–N(3)	82.2(2)	C(1)–C(2)–C(3)	120.6(7)	C(2)–C(3)–C(4)	119.7(8)
N(3)–Cu(2)–O(1)	91.4(2)	Cu(1)–O(3)–C(7)	109.6(4)	C(3)–C(4)–C(5)	120.1(9)	C(4)–C(5)–C(6)	120.5(7)
O(3)–C(7)–N(1)	125.2(7)	O(3)–C(7)–C(6)	117.1(5)	C(17)–C(18)–C(19)	121.4(6)	C(17)–C(18)–C(23)	120.2(7)
C(6)–C(7)–N(1)	117.5(6)	C(7)–N(1)–N(2)	108.4(5)	C(19)–C(18)–C(23)	118.3(7)	C(18)–C(19)–C(20)	120.7(6)
Cu(1)–N(2)–N(1)	114.0(3)	Cu(1)–N(2)–C(8)	127.4(5)	C(19)–C(20)–C(21)	120.1(8)	C(20)–C(21)–C(22)	119.4(8)
N(1)–N(2)–C(8)	118.5(6)	N(2)–C(8)–C(9)	125.5(6)	C(21)–C(22)–C(23)	119.8(7)	C(22)–C(23)–C(18)	121.5(7)
N(3)–Cu(2)–O(1)	91.4(2)	Cu(2)–O(4)–C(17)	109.2(3)				
O(4)–C(17)–N(4)	124.7(6)	O(4)–C(17)–C(18)	117.5(5)	CD(1)–ND–CD(2)	115.9(7)	CD(1)–ND–CD(3)	120.9(8)
C(18)–C(17)–N(4)	117.7(6)	C(17)–N(4)–N(3)	109.7(5)	CD(2)–ND–CD(3)	123.0(8)	ND–CD(3)–OD	124.3(9)
Cu(2)–N(3)–N(4)	114.0(3)	Cu(2)–N(3)–C(16)	127.5(5)				

* Symmetry equivalent position: II $1 - x, -y, 2 - z$.

(1.73 B.M.) expected for $S = \frac{1}{2}$. As the temperature is lowered, the magnetic moment decreases to 0.17 B.M. at 84.6 K. The magnetic susceptibility data were analyzed by the Bleaney–Bowers equation (1) based on the Heisenberg model ($H = -2JS_1S_2$), where each symbol has its usual meaning. The best-fit parameters are $J = -315$ cm^{-1}, $g = 2.05$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. The theoretical curve constructed with these parameters is shown as a solid line in Figure 5. As anticipated from the crystal structure, a fairly good agreement between the experimental and theoretical values is attained. The J value is comparable to those for the complexes of 2,6-bis[*N*-(2-hydroxy-5-substituted phenyl)-iminomethyl]-4-methylphenol, where two copper(II) ions are bridged by an endogenous phenol and an exogenous methoxide oxygen atom.[3d]

$$\chi_A = (Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

Complex (**2**). As the temperature is lowered, the magnetic moment decreases from 1.25 B.M. at 297.8 K to 0.25 B.M. at 87.4 K. The magnetic susceptibility data could be well simulated by equation (1), in spite of the tetranuclear structure. The best fit of the magnetic data to this equation yielded $J = -190$ cm^{-1}, $g = 2.10$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. A comparison of the experimental data with the susceptibilities calculated from the dimer equation is shown in Figure 5. There is good agreement between experimental and calculated values, although the interdimer distances of Cu(2) · · · Cu(2$^{\mathrm{II}}$) and Cu(1)–Cu(2$^{\mathrm{II}}$) are only 3.186(1) and 3.282(1) Å respectively. In the absence of the structural analysis, one might conclude that the complex has a binuclear structure. This result may be interpreted in terms of a predominant interdimer magnetic interaction through the endogenous phenolic oxygen atom O(1), the intra- and interdimer magnetic interactions through the exogenous hydroxide oxygen atom O(2) contributing little to the magnetic susceptibility. There is a difference in the bonding modes of the phenolic and the hydroxide oxygen atoms. As usually found for antiferromagnetic superexchange interaction through bridging oxygen, the phenolic oxygen atom O(1) is bound to three atoms [Cu(1), Cu(2), and C(15)] and has lone-pair electrons. On the other hand, the hydroxide oxygen atom O(2) is bound to four atoms [Cu(1), Cu(2), Cu(2$^{\mathrm{II}}$), and H] and has no lone-pair electrons. A definite theoretical interpretation cannot be made at present, but it is likely that each bond involving the bridging oxygen with sp^3-hybridized orbitals is almost perfectly localized so that no spin-exchange interaction is operative. To our knowledge, the present view can be applied to the all alkoxo-bridged tetranuclear copper(II) complexes so far reported.[11]

References

1 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173; C. J. O'Connor, *ibid.*, 1982, **29**, 203; M. Melnic, *Coord. Chem. Rev.*, 1982, **42**, 259; K. S. Murray, in 'Biological and Inorganic Copper Chemistry,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1987, vol. 2, p. 161; E. Sinn, *ibid.*, p. 195.

2 R. Robson, *Inorg. Nucl. Chem. Lett*, 1970, **6**, 125; *Aust. J. Chem.*, 1970, **23**, 2217.

3 H. Ōkawa, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3019; H. Ōkawa and S. Kida, *ibid.*, 1971, **44**, 1172; H. Ōkawa, S. Kida, Y. Muto, and T. Tokii, *ibid.*, 1972, **45**, 2480; H. Ōkawa, T. Tokii, Y. Nonaka, Y. Muto, and S. Kida, *ibid.*, 1973, **46**, 1462; H. Ōkawa, I. Ando, and S. Kida, *ibid.*, 1974, **47**, 3041.

4 B. F. Hoskins, R. Robson, and H. Schaap, *Inorg. Nucl. Chem. Lett*, 1972, **8**, 21.

5 T. N. Sorrel, D. L. Jameson, and C. J. O'Connor, *Inorg. Chem.*, 1980, **23**, 190.

6 P. Iliopoulos, K. S. Murray, R. Robson, J. Wilson, and G. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1987, 1585.

7 T. Mallah, O. Kahn, J. Gouteron, S. Jeannin, Y. Jeannin, and C. J. O'Connor, *Inorg. Chem.*, 1987, **26**, 1375; P. Guerriero, U. Casellato, D. Ajo, S. Sitran, P. A. Vigato, and R. Graziani, *Inorg. Chim. Acta*, 1988, **142**, 305.

8 (*a*) H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759; (*b*) A. Denton and H. Suschitzky, *J. Chem. Soc.*, 1963, 4741.

9 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Koukoku*, 1979, **55**, 69; S. Kawano, *Rep. Comput. Cent., Univ. Kyushu*, 1980, **13**, 39.

10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

11 V. E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, 1966, **346**, 21; Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem.*, 1976, **38**, 451; V. R. Mergehenn, W. Haase, and R. Allmann, *Acta Crystallogr., Sect. B*, 1975, **31**, 1975; J. A. Bertrand and J. A. Kelly, *Inorg. Chim. Acta*, 1970, **4**, 203; N. Matsumoto, T. Tsutsumi, A. Ohyoshi, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1388.

Received 16*th December* 1988; *Paper* 8/04948C