Synthesis, Structure, and Spectral and Magnetic Properties of Trinuclear Copper(II) Complexes bridged by Glyoximate Groups[†]

Hisashi Ōkawa,* Masayuki Koikawa, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan
Dominique Luneau and Hiroki Oshio
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Copper(II) complexes of composition $Cu_3L_2L'_2(ClO_4)_2$ or $Cu_3L_2L'_2(CH_3OH)_2(NO_3)_2$ were obtained where L = dimethylglyoximate (dmg), diphenylglyoximate (dpg), or *o*-benzoquinone dioximate (bqd) dianion, L′ = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen). The crystal structures of $Cu_3(dmg)_2(bipy)_2(CH_3OH)_2(NO_3)_2$ and $Cu_3(dpg)_2(bipy)_2(CH_3OH)_2(NO_3)_2$ were solved by the single-crystal *X*-ray method. Both have an essentially similar trinuclear structure where the $[CuL_2]^{2-}$ dianion functions as a bridge between two copper(II) ions through its deprotonated oximate oxygens. The configuration around the central copper (with two L^{2-} ions) is an elongated octahedron with two NO_3^- ions above and below the $[CuL_2]^{2-}$. The configuration around the terminal copper is a square pyramid with two nitrogens of bipy and two oxygens of oximate groups in the basal plane and the methanol oxygen at the apical site. Cryomagnetic investigations (80—300 K) revealed the operation of a very strong antiferromagnetic spin exchange through the oximate bridges, causing complete or nearly complete spin coupling even at room temperature. Exchange integrals ($-J$) larger than 300 cm^{-1} were evaluated for all the complexes. Based on e.s.r. spectra in methanol, it is suggested that the unpaired electron is localized on the terminal copper atom. The complexes dimerized in dimethylformamide, especially at a low temperature, and their frozen solutions each showed an e.s.r. spectrum typical of the spin-triplet state.

It is known that the oximate group ($=N-O^-$) can function as a bridge[1] between two metal ions through the imino nitrogen and the deprotonated oxygen, to afford bi-and tri-nuclear complexes.[2–12] Typical examples are binuclear copper(II) complexes with double oximate bridges in *trans* arrangement[2–8] [type (**A**) in Figure 1] and triangular trinuclear copper(II) complexes with peripheral oximate bridges [type (**B**)].[2,9–12] In these types of complexes the oximate group generally mediates a strong antiferromagnetic spin exchange and a complete or nearly complete spin coupling has been attained in some cases even at room temperature.[4,5,9] Another type of trinuclear copper(II) complexes with double oximate bridges in *cis* arrangement [type (**C**)] may be obtained by the use of glyoximate ligands. The synthesis of this type was first attempted by Singh and Sahoo[13] using dimethylglyoxime (H_2dmg) and acetylacetone dioxime. They obtained copper(II) complexes such as $[Cu(Hdmg)_2(CuCl_2)_2]$, $[\{Cu(Hdmg)_2\}_2Cu(NO_3)_2]$, and $[Cu(Hdmg)_2\{Cu(H_2O)\}_2Br_4]$, which were presumed to be trinuclear on the basis of cryomagnetic investigations. I.r. spectral and elemental analytical data for those complexes, however, suggested the presence of O–H groups, presumably attributable to that of $[Cu(Hdmg)_2]$. Therefore, the glyoximate-bridged trinuclear structure supposed for those complexes has not been definitely elucidated.

In this study we have carried out the synthesis of type (**C**) complexes with dimethylglyoximate ion (dmg^{2-}), diphenylglyoximate ion (dpg^{2-}), or *o*-benzoquinone dioximate ion (bqd^{2-}) as the bridging ligand and 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) as an end-cap ligand. This paper deals with the synthesis, structure, electronic spectra, magnetism, and e.s.r. spectra of trinuclear copper(II) complexes of general formula $Cu_3L_2L'_2(ClO_4)_2$ or $Cu_3L_2L'_2(CH_3OH)_2(NO_3)_2$ (L = dmg^{2-}, dpg^{2-}, or bqd^{2-}; L′ = bipy or phen). A part of this work was preliminarily reported.[14]

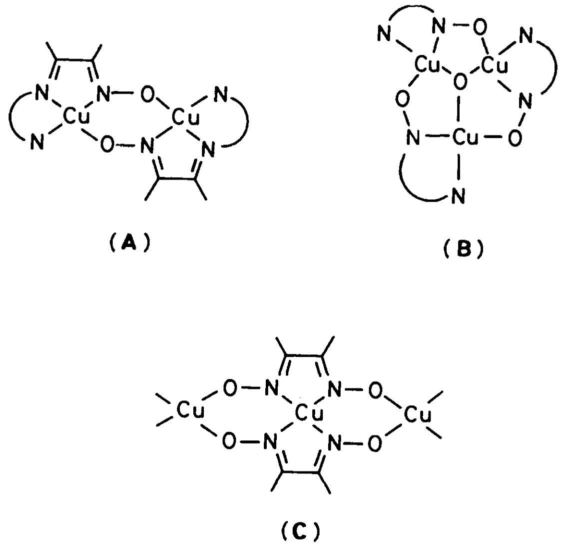

Figure 1. Chemical structures of oximate-bridged complexes

Experimental

Materials.—2,2′-Bipyridyl and 1,10-phenanthroline were purchased from Wako Chemical Co. and H_2dmg and H_2dpg from Tokyo Kasei Chemical Co., H_2bqd was prepared by the literature method.[15] The complexes $[Cu(Hdmg)_2]$, $[Cu(Hdpg)_2]$, and $[Cu(Hbqd)_2]$ were prepared by the reaction

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Elemental analyses (%) of trinuclear complexes

	Found				Calc.			
Complex	C	H	N	Cu	C	H	N	Cu
(1)	39.15	3.95	15.45	20.35	39.20	3.95	15.25	20.75
(2)	35.95	3.00	12.10	20.30	36.15	3.05	12.05	20.50
(3)	39.20	2.95	11.50	18.70	39.30	2.90	11.45	19.50
(4)	50.45	3.55	12.35	16.45	51.45	3.80	12.00	16.35
(5)	42.30	3.20	14.60	19.50	42.40	3.25	14.35	19.80

Table 2. Summary of crystal data, intensity-data collection, and structure refinements *

Complex	(1)	(4)
Formula	$C_{30}H_{36}Cu_3N_{10}O_{12}$	$C_{50}H_{48}Cu_3N_{10}O_{14}$
M	919.29	1 203.57
Crystal system	Triclinic	Triclinic
a/Å	11.732(8)	12.114(7)
b/Å	12.037(9)	12.757(8)
c/Å	8.618(4)	9.817(2)
α/°	112.82(5)	82.31(4)
β/°	92.27(6)	100.54(3)
γ/°	119.50(5)	119.09(5)
U/Å^3	905.4(1)	1 301.6(1)
D_c/g cm^{-3}	1.693	1.536
D_m/g cm^{-3}	1.702	1.583
μ(Mo-K_α)/cm^{-1}	18.93	13.42
Crystal size (mm)	0.43 × 0.22 × 0.16	0.48 × 0.44 × 0.15
T/K	293	250
$2\theta_{max.}$/°	50	60
No. of reflections measured	5 528	7 079
No. of unique reflections with [$\lvert F_o\rvert > 3\sigma(F_o)$]	2 801	4 836
No. of reflections per parameter	8.7	11.5
Maximum, minimum residual electron density (e Å^{-3})	1.8, −1.6	0.7, −0.9
Maximum shift/e.s.d.	0.3	0.5
Weighting scheme (w)	$[\sigma_c^2 + (0.03\lvert F\rvert)^2]^{-1}$	$[\sigma_c^2 + (0.03\lvert F\rvert)^2]^{-1}$
R	0.038	0.044
R'	0.049	0.060

* Details in common: crystal system, triclinic; space group $P\bar{1}$; $Z = 1$; Rigaku AFC-5 diffractometer; scan type θ—2θ; scan width 1.2 + 0.4 tanθ; scan speed 3° min^{-1}; octant measured, $+h, \pm k, \pm l$.

Table 3. Positional parameters for complex (1)

Atom	x	y	z
Cu(1)	0	0	0
Cu(2)	0.273 71(3)	0.381 24(3)	0.089 53(5)
O(1)	0.308 2(2)	0.260 7(2)	0.147 4(3)
O(2)	0.083 9(2)	0.245 8(2)	−0.079 7(3)
N(1)	0.209 2(2)	0.132 3(2)	0.134 5(3)
N(2)	−0.018 6(2)	0.121 8(2)	−0.088 5(3)
N(3)	0.485 2(2)	0.548 3(2)	0.225 0(3)
N(4)	0.290 7(3)	0.526 1(3)	0.009 6(3)
C(1)	0.255 2(3)	0.075 6(3)	0.200 1(4)
C(2)	0.407 7(3)	0.146 4(4)	0.287 6(5)
C(3)	−0.145 3(3)	0.063 8(3)	−0.185 3(4)
C(4)	−0.178 0(3)	0.130 6(4)	−0.280 9(5)
C(5)	0.577 8(3)	0.550 0(3)	0.332 4(4)
C(6)	0.719 8(3)	0.665 4(4)	0.416 4(4)
C(7)	0.767 7(3)	0.780 8(3)	0.384 8(4)
C(8)	0.674 2(3)	0.781 4(3)	0.273 7(4)
C(9)	0.530 7(3)	0.663 1(3)	0.197 0(4)
C(10)	0.421 0(3)	0.653 6(3)	0.081 2(4)
C(11)	0.444 5(3)	0.763 0(3)	0.043 9(5)
C(12)	0.332 9(4)	0.741 9(4)	−0.068 0(5)
C(13)	0.202 0(4)	0.610 9(4)	−0.142 7(5)
C(14)	0.185 0(3)	0.507 5(4)	−0.099 6(5)
N(n)	−0.112 8(3)	0.160 7(3)	0.292 2(4)
O(n1)	−0.054 7(3)	0.098 3(3)	0.290 7(4)
O(n2)	−0.240 5(3)	0.095 0(3)	0.250 9(5)
O(n3)	−0.039 9(3)	0.294 2(3)	0.339 5(5)
C(m)	0.216 7(4)	0.604 4(4)	0.389 2(6)
O(m)	0.217 3(3)	0.480 2(3)	0.338 0(4)

of a copper(II) salt and a ligand in the 1 : 2 mol ratio in methanol.[16] The nitrate and perchlorate salts of bis(2,2′-bipyridyl)copper(II) and bis(1,10-phenanthroline)copper(II) were obtained by the literature methods.[17,18]

Preparation of Complexes.—The following trinuclear complexes have been obtained: $Cu_3(dmg)_2(bipy)_2(CH_3OH)_2(NO_3)_2$ (**1**), $Cu_3(dmg)_2(bipy)_2(ClO_4)_2$ (**2**), $Cu_3(dmg)_2(phen)_2(ClO_4)_2$ (**3**), $Cu_3(dpg)_2(bipy)_2(CH_3OH)_2(NO_3)_2 \cdot 2H_2O$ (**4**), and $Cu_3(bqd)_2(bipy)_2(CH_3OH)_2(NO_3)_2$ (**5**). Two different synthetic methods were adopted as exemplified below.

Method (*a*). A mixture of $[Cu(bipy)_2][NO_3]_2 \cdot H_2O$ (796 mg, 2 × 10^{-3} mol) and $[Cu(Hdmg)_2]$ (294 mg, 1 × 10^{-3} mol) in absolute methanol (50 cm^3) was gently refluxed for 2 h. Black-purple prisms thus formed were collected by filter suction and recrystallized from methanol.

Method (*b*). A mixture of $[Cu(Hdmg)_2]$ (294 mg, 1 × 10^{-3} mol), 2,2′-bipyridyl (312 mg, 2 × 10^{-3} mol), and copper(II) nitrate trihydrate (483 mg, 2 × 10^{-3} mol) in absolute methanol (40 cm^3) was stirred under gentle reflux for 3 h, and the resulting black-purple crystals were treated as described in method (*a*).

Analytical data for the complexes obtained are given in Table 1.

X-Ray Structural Determination.—Single crystals of the complexes (**1**) and (**4**) suitable for *X*-ray crystallographic analysis were grown by slow diffusion. Crystal parameters and details of the data collection and refinements are given in Table 2. Intensity data were collected at room temperature for complex (**1**) and at 250 K for complex (**4**) on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

The data were reduced by the use of the UNICS III program system of the Computer Center of the Institute for Molecular Science. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. Atomic scattering factors were taken from ref. 19. The hydrogen atoms were located by Fourier difference-synthesis and included in the least-squares calculation.

Positional parameters of non-hydrogen atoms for the complexes (**1**) and (**4**) are given in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Other Physical Measurements.—Magnetic susceptibilities of powder samples were determined by the Faraday method in the range from liquid-nitrogen temperature to room temperature. The apparatus was calibrated with $[Ni(en)_3][S_2O_3]$.[20] The magnetic moments were calculated from the equation $\mu_{eff.} = 2.828(\chi_M T)^{\frac{1}{2}}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism of the constituent atoms by the use of Pascal's constants. Infrared spectra were recorded on a JASCO IR-810 spectrometer for KBr discs or Nujol mulls,

Table 4. Positional parameters for complex (**4**)

Atom	*x*	*y*	*z*
Cu(1)	0	0	0
Cu(2)	0.346 35(3)	0.084 06(3)	0.058 11(4)
O(1)	0.209 4(2)	−0.064 0(2)	0.115 4(2)
O(2)	0.262 5(2)	0.145 7(2)	−0.087 7(2)
N(1)	0.091 1(2)	−0.083 8(2)	0.114 0(3)
N(2)	0.143 8(2)	0.128 4(2)	−0.094 8(2)
N(3)	0.467 3(2)	0.024 6(2)	0.167 3(3)
N(4)	0.515 3(2)	0.215 5(2)	0.003 5(3)
C(1)	0.019 2(3)	−0.176 5(2)	0.188 6(3)
C(2)	0.065 2(3)	−0.255 0(3)	0.277 0(3)
C(3)	0.135 8(4)	−0.218 9(4)	0.405 3(4)
C(4)	0.177 1(5)	−0.293 2(5)	0.490 0(5)
C(5)	0.147 8(5)	−0.402 7(4)	0.447 6(5)
C(6)	0.080 7(5)	−0.437 6(4)	0.320 4(5)
C(7)	0.037 8(4)	−0.364 2(3)	0.235 6(4)
C(8)	0.113 6(2)	0.201 1(2)	−0.177 5(3)
C(9)	0.208 8(3)	0.306 6(2)	−0.254 1(3)
C(10)	0.294 5(4)	0.408 3(3)	−0.183 2(4)
C(11)	0.385 5(4)	0.507 9(3)	−0.252 5(5)
C(12)	0.390 0(4)	0.504 8(3)	−0.389 5(5)
C(13)	0.305 0(4)	0.405 1(4)	−0.459 3(4)
C(14)	0.213 9(4)	0.306 1(3)	−0.392 1(4)
C(15)	0.431 3(3)	−0.079 1(3)	0.245 6(3)
C(16)	0.518 5(4)	−0.116 2(4)	0.310 3(4)
C(17)	0.644 4(4)	−0.046 7(4)	0.295 0(4)
C(18)	0.683 2(3)	0.061 2(4)	0.213 3(4)
C(19)	0.592 3(3)	0.094 4(3)	0.151 6(3)
C(20)	0.619 6(3)	0.205 4(3)	0.063 6(3)
C(21)	0.741 6(3)	0.293 9(4)	0.040 9(4)
C(22)	0.755 4(3)	0.394 8(4)	−0.043 0(5)
C(23)	0.648 3(4)	0.403 3(3)	−0.105 0(4)
C(24)	0.530 5(3)	0.312 1(3)	−0.079 6(4)
N(n)	0.080 3(3)	0.247 9(3)	0.170 4(3)
O(n1)	0.042 0(4)	0.138 8(2)	0.191 0(3)
O(n2)	0.014 8(4)	0.294 7(4)	0.155 9(6)
O(n3)	0.194 3(3)	0.310 7(3)	0.159 0(4)
O(m)	0.346 0(2)	0.199 4(2)	0.218 5(3)
C(m)	0.340 3(6)	0.152 5(5)	0.357 6(4)
O(w)	0.948 9(6)	0.010 8(7)	0.462 3(10)

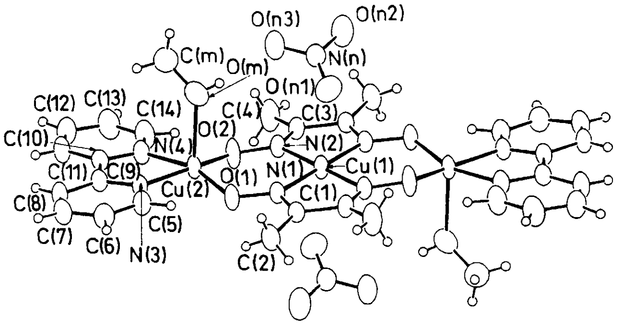

Figure 2. Molecular structure of complex (**1**) and its numbering system

electronic spectra on a Hitachi 3400 UV spectrometer in dimethylformamide (dmf), and *X*-band e.s.r. spectra on a JES-FE3X spectrometer for powder samples and in dmf or methanol solutions.

Results and Discussion

Preparation.—The nitrate salts of the trinuclear complexes were synthesized either by the reaction of $[Cu(HL)_2]$ (HL = dioxime) and $[Cu(bipy)_2][NO_3]_2$ {or $[Cu(phen)_2][NO_3]_2$} in the 1:2 mol ratio in methanol [method (*a*)] or by the reaction of $[Cu(HL)_2]$, copper(II) nitrate trihydrate, and an end-cap ligand (bipy or phen) in the 1:2:2 mol ratio in methanol [method (*b*)]. The perchlorate salts, on the other hand, could be synthesized only by method (*b*). The nitrate salts (**1**), (**4**), and (**5**) were obtained as the adducts of two methanol molecules while the perchlorate salts (**2**) and (**3**) were obtained as the solvent-free form. All the complexes are deeply coloured (black or black purple) and are stable to the atmosphere.

The success in synthesis of the trinuclear complexes seems to depend upon the choice of the 'end-cap' ligand. The use of bipy or phen as the end-cap ligand gave the desired complexes in tolerable yields whereas our efforts to synthesize trinuclear complexes with ethylenediamine, pentane-2,4-dionate ion, or diethylenetriamine as the end-cap ligand were in vain.

It is known that planar $[M(bipy)_2]^{2+}$ and $[M(phen)_2]^{2+}$ complexes are distorted from the rigid square-planar configuration because of interligand steric repulsion within each molecule.[21,22] In the case of copper(II) complexes this usually results in five-co-ordinate or distorted six-co-ordinate species.[23] Further, because of this, one of the bipy or phen ligands tends to be replaced with another ligand to afford ternary complexes,[24] and in special cases dihydroxo-bridged binuclear[25] and imidazolate-bridged trinuclear[26] copper(II) complexes have been obtained by taking advantage of this steric effect. In the present case the same steric effect must contribute to the facile formation of the type (**C**) complexes with bipy or phen as the end-cap ligand. The complexes show no i.r. band attributable to ν(O–H) vibration in the region 1 600—2 000 cm^{-1},[27] indicating that all dioxime oxygens are deprotonated to afford the $[CuL_2]^{2-}$ anion.

Crystal Structures.—*Complex* (**1**). A perspective drawing of the structure is given in Figure 2 together with the numbering system. Relevant bond distances and angles with estimated standard deviations are given in Table 5.

The complex molecule consists of a trinuclear cation and nitrate ions and has the inversion centre at the central copper Cu(1). The $[Cu(dmg)_2]^{2-}$ dianion bridges two copper ions through its deprotonated oxime oxygens with a Cu(1) ··· Cu(2) separation of 3.754(2) Å. The Cu(1)–N(1) and Cu(1)–N(2) bond distances are 2.000(3) and 1.981(4) Å, respectively, which are slightly longer than those (1.91—1.96 Å) of $[Cu(Hdmg)_2]$.[28] The nitrate ions are located on each side of the CuN_4 plane and the shortest Cu(1)–O(n1) distance is 2.613(3) Å. Thus, the configuration around the central copper may be described as an elongated octahedron.

Each terminal copper atom Cu(2) is in a distorted square-pyramidal environment with two nitrogen atoms of bipy and two oximate oxygens in the basal plane and the oxygen atom of a methanol molecule at the apical site. The Cu(2)–N(3) and Cu(2)–O(1) distances [2.048(3) and 1.901(3) Å, respectively] are common for in-plane co-ordination of copper(II), whereas the Cu(2)–O(*m*) distance [2.356(4) Å] is elongated. The deviation of Cu(2) from the basal N_2O_2 plane is very small [0.184(1) Å] and the trinuclear skeleton is nearly coplanar. A prominent structural difference between the $[Cu(dmg)_2]^{2-}$ moiety of the trinuclear complex and $[\{Cu(Hdmg)_2\}_2]$[28] is seen in the O(1) ··· O(2) separation. The separation in the former (with O–M–O bonding) is 2.986(4) Å whereas the separation in the latter (with hydrogen bonding) is 2.53—2.70 Å.

Complex (**4**). Perspective drawings of the structure with the

Table 5. Relevant bond distances (Å) and angles (°) for complex (**1**)

Cu(1)–N(1)	2.000(3)	Cu(1)–N(2)	1.981(4)
Cu(2)–O(1)	1.901(3)	Cu(2)–O(2)	1.902(3)
Cu(2)–N(3)	2.048(3)	Cu(2)–N(4)	2.044(4)
Cu(1)–O(n1)	2.613(3)	Cu(2)–O(m)	2.356(4)
Cu(1) ··· Cu(2)	3.754(2)	O(1) ··· O(2)	2.986(4)
N(1)–Cu(1)–N(2)	99.3(1)	N(1)–Cu(1)–N(2$^{\rm I}$)	80.7(1)
O(1)–Cu(2)–O(2)	103.6(1)	O(1)–Cu(2)–N(3)	88.2(1)
O(1)–Cu(2)–N(4)	162.5(1)	O(1)–Cu(2)–O(m)	99.3(1)
O(2)–Cu(2)–N(3)	164.6(1)	O(2)–Cu(2)–N(4)	87.0(1)
O(2)–Cu(2)–O(m)	94.8(1)	N(3)–Cu(2)–N(4)	79.3(1)
O(1)–N(1)–Cu(1)	129.7(1)	O(2)–N(2)–Cu(1)	128.6(1)
N(1)–O(1)–Cu(2)	125.8(2)	N(2)–O(2)–Cu(2)	126.5(3)

Superscript I indicates the equivalent position, $-x,-y,-z$.

Table 6. Relevant bond distances (Å) and angles (°) of complex (**4**)

Cu(1)–N(1)	1.997(3)	Cu(1)–N(2)	1.999(3)
Cu(2)–O(1)	1.909(2)	Cu(2)–O(2)	1.909(3)
Cu(2)–N(3)	2.040(3)	Cu(2)–N(4)	2.028(3)
Cu(1)–O(n1)	2.565(4)	Cu(2)–O(m)	2.296(3)
Cu(1) ··· Cu(2)	3.741(2)	O(1) ··· O(2)	2.986(4)
N(1)–Cu(1)–N(2)	99.1(1)	N(1)–Cu(1)–N(2$^{\rm I}$)	80.9(1)
O(1)–Cu(2)–O(2)	102.9(1)	O(1)–Cu(2)–N(3)	87.3(1)
O(1)–Cu(2)–N(4)	165.2(1)	O(2)–Cu(2)–N(3)	162.5(1)
O(1)–Cu(2)–O(m)	96.7(1)	O(2)–Cu(2)–O(m)	92.5(1)
O(2)–Cu(2)–N(4)	88.3(1)	N(3)–Cu(2)–N(4)	79.5(1)
O(1)–N(1)–Cu(1)	129.3(2)	O(2)–N(2)–Cu(1)	129.1(2)
N(1)–O(1)–Cu(2)	125.1(2)	N(2)–O(2)–Cu(2)	125.3(2)

Superscript I indicates the equivalent position $-x,-y,-z$.

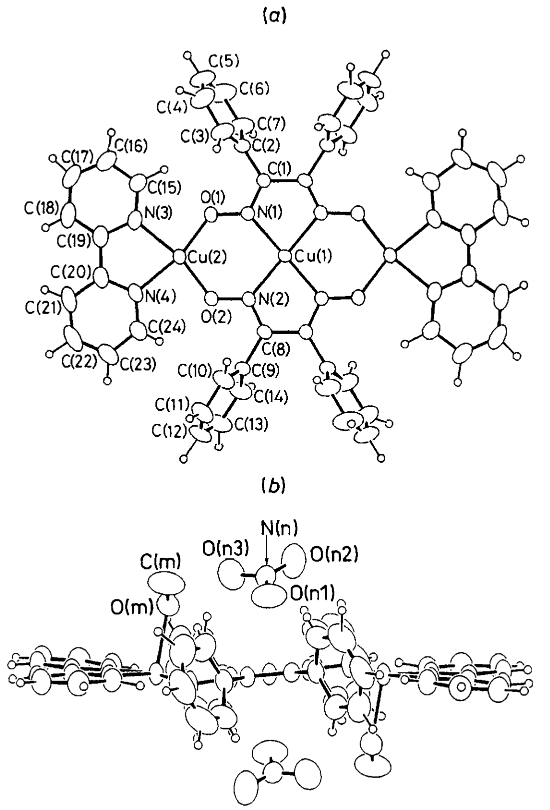

Figure 3. Perspective drawings of complex (**4**) and its numbering system: (*a*) projection on the copper co-ordination plane and (*b*) edge-on-view

numbering system are given in Figure 3. The relevant bond distances and angles are given in Table 6.

The structure is essentially similar to that of complex (**1**) and has the inversion centre at the central copper Cu(1). The Cu(1) ··· Cu(2) separation is 3.741(2) Å that is larger than that of complex (**1**). The configuration around Cu(1) is an elongated octahedron with the nitrate ions above and below the equatorial plane formed by the dpg ligands [see Figure 3(*b*)]. The shortest Cu(1)–O(n1) bond distance is 2.565(4) Å. The configuration around the terminal copper Cu(2) is a distorted square pyramid with two nitrogens of bipy and two oxygens of the oximate groups in the basal plane and the methanol oxygen O(m) at the apex. The Cu(2)–O(m) bond distance is 2.296(3) Å. Two water molecules involved are captured in the crystal lattice. It is seen that the axial Cu(1)–O(n1) and Cu(2)–O(m) bond distances are both slightly shorter than the corresponding bond distances of complex (**1**). Instead, the in-plane bond distances are slightly elongated for both Cu(1) and Cu(2). The O(1) ··· O(2) separation [2.986(4) Å] is much elongated by the co-ordination to Cu(2) compared with the corresponding O ··· O separations for $[Ni(Hdpg)_2]^+$[29] (2.40 Å) and $[Pd(Hdpg)_2]^+$[30] (2.63 Å). The trinuclear skeleton except for the phenyl rings of the dpg ligands forms a close coplane. The phenyl rings are nearly perpendicular to the trinuclear skeleton. The dihedral angle formed by the phenyl ring and the CuN_4 least-squares plane is 78.7(2)° for the phenyl ring attached to C(1) and 77.5(1)° for the phenyl ring attached to C(8). The dihedral angles in the present complexes are significantly larger compared with that (36.8°) of $[Ni(Hdpg)_2]^+$.[29]

Electronic Spectra.—Electronic spectra of the complexes were determined in dmf in the range 10 000—37 000 cm^{-1} and were found to obey Beer's law above 1×10^{-4} mol dm^{-3}. The spectrum of complex (**1**) is given in Figure 4 and the numerical data are summarized in Table 7. Electronic spectra of $[Cu(Hdmg)_2]$ and $[NiL''Cu(bipy)][ClO_4]_2$* (H_2L'' = the 1:2 condensation product of 1,3-diaminopropane and biacetyl mono-oxime) were also measured as the references and included in Figure 4. The latter complex has the chemical structure shown in Figure 5 and its copper is compared to the terminal copper of the trinuclear complexes.

The trinuclear complexes each showed distinct absorption bands near 21 000, 29 000, 32 000—34 000, and 34 000—38 000 cm^{-1}. Of particular interest is the first of these of significant intensity (ε >4 000 dm^3 mol^{-1} cm^{-1}). A similar band was seen in reflectance spectra of the complexes. Such a strong absorption was not recognized for $[Cu(Hdmg)_2]$ in chloroform.[3] Our spectral investigations of $[Cu(Hdmg)_2]$ in dmf also revealed that this complex does not show any intense absorption band below 30 000 cm^{-1} in this solvent. Orange $[NiL''Cu(bipy)][ClO_4]_2$ shows a significantly intense absorption band at 26 300 cm^{-1} but no intense absorption below 25 000 cm^{-1}. Thus, the glyoximate-bridged trinuclear copper(II) complexes are characterized by an intense absorption at 21 000 cm^{-1}, though the assignment of the band remains to be studied. The *d–d* transition bands of the copper(II) ions are concealed by the band at 21 000 cm^{-1} and barely observed as a discernible shoulder near 17 000 cm^{-1}. Two absorptions above 30 000 cm^{-1} may be attributed to the intraligand transitions of the end-cap ligand. In Figure 4 the intensities of the bands at 32 000 and

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* This complex was obtained by the reaction of $[NiL'']ClO_4$, copper(II) perchlorate hexahydrate, bipy, and NaOH in methanol: $\mu_{\rm eff.}$ per NiCu = 1.84 μ_B. Detailed physicochemical properties will be reported elsewhere together with those of related complexes.

Table 7. Electronic spectra data in dmf

Complex		$10^{-3}\tilde{\nu}/\text{cm}^{-1}$ ($\varepsilon/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$)			
(**1**)	17 (sh)	21.2 (4 490)	29 (10 900)	32.2 (34 000)	34.0 (43 100)
(**2**)	17 (sh)	21.1 (4 260)	29 (10 700)	32.2 (32 600)	33.9 (40 300)
(**3**)	18 (sh)	21.0 (4 010)	28.6 (6 980) 29.9 (8 570)	34.2 (23 800)	37.8 (43 800)
(**4**)	17 (sh)	21.6 (5 140)	28 (12 300)	32.4 (33 300)	34.3 (52 600)
(**5**)	17 (sh)	21.4 (13 990)	26.8 (15 200) 29.8 (15 560)	32.1 (38 700)	33.6 (47 600)

Absorption coefficients are given per molecule; sh = shoulder.

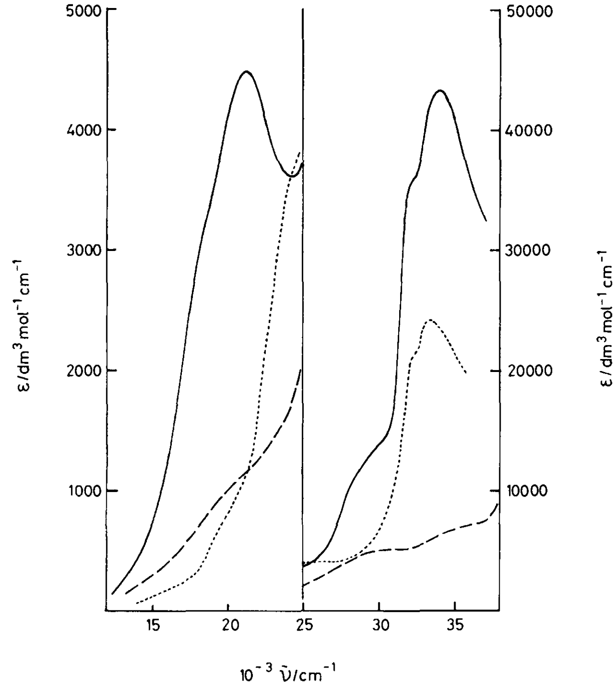

Figure 4. Electronic spectra of (——) complex (**1**), (— — —) $[Cu(Hdmg)_2]$, and (· · ·) $[NiL''Cu(bipy)][ClO_4]_2$ in dmf (HL″ = the 1:2 condensation product of 1,3-diaminopropane and biacetyl monooxime)

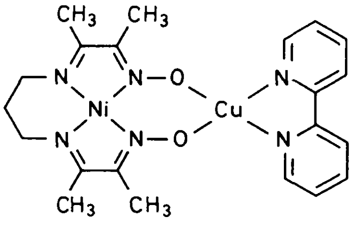

Figure 5. Chemical structure of $[NiL''Cu(bipy)]^{2+}$

34 000 cm^{-1} of complex (**1**) are approximately twice of those of the corresponding bands of $[NiL''Cu(bipy)][ClO_4]_2$, in accord with the numbers of bipy ligands involved in the complex molecules.

Table 8. Effective magnetic moments of complexes (per molecule) near liquid-nitrogen temperature and at room temperature

Complex	$\mu_{\text{eff.}}/\mu_B$ (T/K)	
(**1**)	1.84 (85.8)	1.85 (297.8)
(**2**)	1.84 (85.2)	1.87 (297.3)
(**3**)	1.82 (83.6)	1.84 (297.3)
(**4**)	1.80 (84.6)	1.83 (297.8)
(**5**)	1.85 (84.0)	1.88 (297.4)

Magnetic Properties.—All the complexes show a subnormal magnetic moment ($\approx 1.1\ \mu_B$ per metal atom) at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule. Magnetic susceptibilities were measured over the temperature range 80—300 K and it was found that the moment of each complex is practically independent of temperature in the range examined. When the magnetic moments are calculated per three copper atoms, the moments correspond well to the spin-only value expected for one unpaired electron. The result clearly indicates that the spin-exchange interaction in these complexes is very strong so that a complete or nearly complete spin coupling is attained even at room temperature. The magnetic moments of the complexes (per molecule) at room temperature and near liquid-nitrogen temperature are given in Table 8. It seems that the co-ordination or non-co-ordination of a methanol molecule at the terminal copper gives rise to no essential effect upon the magnetic property.

Based on the Heisenberg model $\mathscr{H} = -2\Sigma(J_{ij}\hat{S}_i\hat{S}_j)$ and according to Kambe's procedure,[32] two spin-doublet states $S_T = \frac{1}{2}\ (S_{23} = 0)$ and $S_T = \frac{1}{2}\ (S_{23} = 1)$ and one spin-quartet state $S_T = \frac{3}{2}$ occur for linear Cu^2–Cu^1–Cu^3, where $\hat{S}_T = \hat{S}_1 + \hat{S}_2 + \hat{S}_3$ and $\hat{S}_{23} = \hat{S}_2 + \hat{S}_3$. Assuming that the exchange integrals between the neighbouring copper ions are identical ($J_{12} = J_{13} = J$) and the integral between the terminal copper ions is zero ($J_{23} = 0$), the $S_T = \frac{1}{2}\ (S_{23} = 0)$ state is $-2J$ above the ground state $S_T = \frac{1}{2}\ (S_{23} = 1)$ and the $S_T = \frac{3}{2}$ state is $-3J$ above the ground state. Complete or nearly complete spin coupling at room temperature means a $-3J$ value of *ca.* 1 000 cm^{-1}. Therefore, we may conclude that the $-J$ value is larger than 300 cm^{-1} for all the complexes. It should be mentioned that the trinuclear complexes of Singh and Sahoo,[13] $[Cu(Hdmg)_2\{CuCl_2\}_2]$ $[\{Cu(Hdmg)_2\}_2Cu(NO_3)_2]$, and $[Cu(Hdmg)_2\{Cu(H_2O)\}_2Br_4]$, showed a much weaker spin exchange: their $-J$ values were reported to be 91, 175, and 49 cm^{-1}, respectively. It is shown from the present study that the oximate group can mediate a very strong antiferromagnetic spin exchange in doubly bridged dicopper(II) systems in the *cis* as well as the *trans* arrangement.

E.S.R. Spectra.—As shown above the present complexes exhibit a very rare situation where one unpaired electron exists per three copper nuclei. Their e.s.r. spectra are interesting in relation to the spectra of the mixed-valence dicopper(I,II)[33—36] and dicopper(II,III)[33,37] complexes that possess one unpaired electron per two copper atoms. The e.s.r. spectra of complexes (**1**)—(**5**) were recorded on powder samples and in dmf or methanol solutions (concentration: *ca.* 5 × 10^{-4} mol dm^{-3}) at various temperatures. Typical spectra are given in Figures 6 and 7 and numerical data are summarized in Table 9.

When measured on powder samples at room temperature each spectrum showed an axially symmetric pattern with $g_{\parallel}$ = 2.21—2.23 and $g_{\perp}$ = 2.06—2.07 [Figure 6(*a*)]. No hyperfine structure was resolved for both $g_{\parallel}$ and $g_{\perp}$ components even at 10 K. It should be noted that these spectral features resemble those of monomeric copper(II) of axial symmetry.

Table 9. E.s.r. parameters of the complexes

			dmf	
Complex	Powder sample	Methanol solution	Solution	Frozen solution
(1)	$g_{\parallel} = 2.23$ $g_{\perp} = 2.07$	$g_{av.} = 2.118$ $A_{av.} = 0.0072$ ($g' = 4.24$)	$g_{av.} = 2.106$ ($g' = 4.23$)	$g_{\parallel} = 2.245$ $A_{\parallel} = 0.009\,96$ $g_{\perp} = 2.061$ $g' = 4.169$
(2)	$g_{\parallel} = 2.21$ $g_{\perp} = 2.07$	$g_{av.} = 2.112$ $A_{av.} = 0.0072$ ($g' = 4.19$)	$g_{av.} = 2.109$ ($g' = 4.20$)	$g_{\parallel} = 2.240$ $A_{\parallel} = 0.009\,84$ $g_{\perp} = 2.064$ $g' = 4.170$
(3)	$g_{\parallel} = 2.20$ $g_{\perp} = 2.06$	$g_{av.} = 2.113$ $A_{av.} = 0.0071$ ($g' = 4.19$)	$g_{av.} = 2.105$ ($g' = 4.19$)	$g_z = 2.20$ $g_x = 2.06$ $g_y = 1.94$ $g' = 4.187$
(4)	$g_{\parallel} = 2.23$ $g_{\perp} = 2.06$	$g_{av.} = 2.112$ $A_{av.} = 0.0072$ ($g' = 4.20$)	$g_{av.} = 2.109$ ($g' = 4.20$)	$g_{\parallel} = 2.240$ $A_{\parallel} = 0.0100$ $g_{\perp} = 2.066$ $g' = 4.190$
(5)	$g_{\parallel} = 2.22$ $g_{\perp} = 2.06$	$g_{av.} = 2.115$ $A_{av.} = 0.0072$ ($g' = 4.21$)	$g_{av.} = 2.108$ ($g' = 4.23$)	$g_{\parallel} = 2.240$ $A_{\perp} = 0.0099$ $g_{\perp} = 2.055$ $g' = 4.177$

Hyperfine coupling constants are given in cm^{-1}. Values in parentheses were for weak signals.

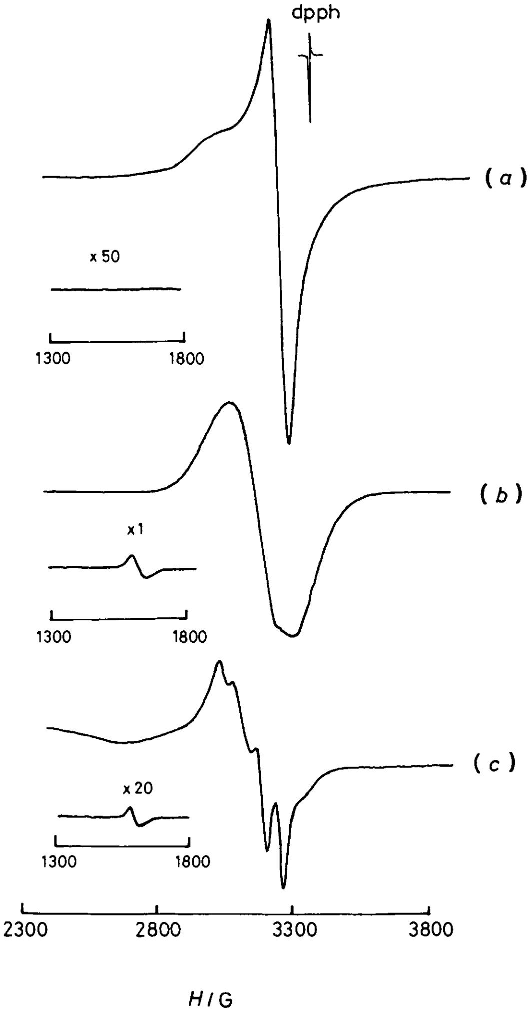

Figure 6. *X*-Band e.s.r. spectra of complex (**1**) at room temperature: (*a*) powder sample, (*b*) in dmf, and (*c*) in methanol

In dmf solutions at room temperature each complex showed one broad band at $g \approx 2.11$ [Figure 6(*b*)]. We also measured the spectra in this solvent at temperatures up to 418 K, but the band became more broad above 350 K.

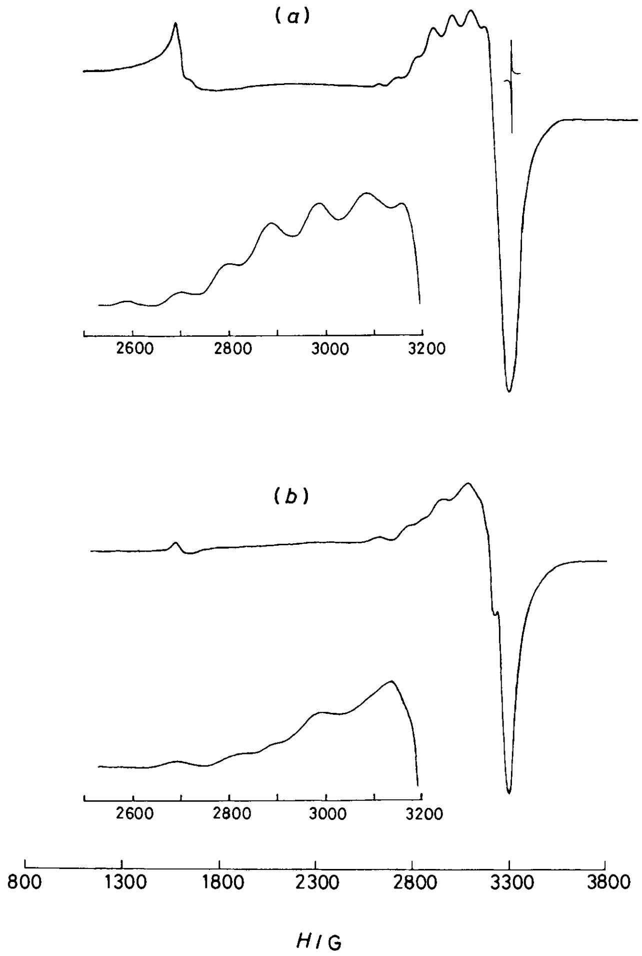

Figure 7. E.s.r. spectra of complex (**1**) in frozen dmf solution (*a*) and frozen methanol solution (*b*)

In methanol at room temperature, on the other hand, each complex showed an isotropic e.s.r. signal with four-line hyperfine structure [$g_{av.} = 2.112$—2.118 and $A_{av.} = (71$—$72) \times 10^{-4}$ cm^{-1}] [see Figure 6(*c*)]. This spectral feature was maintained up to 323 K. Such e.s.r. spectra in methanol imply that the unpaired electron is localized on one copper atom.

In order to specify the copper site on which the unpaired electron resides, we have examined e.s.r. spectra of $[\mathrm{Cu(Hdmg)_2}]$ and $[\mathrm{NiL''Cu(bipy)}][\mathrm{ClO_4}]_2$ in methanol at room temperature. The complex $[\mathrm{Cu(Hdmg)_2}]$ showed an isotropic e.s.r. signal of $g_{\mathrm{av.}} = 2.075$ and $A_{\mathrm{av.}} = 76 \times 10^{-4}$ cm^{-1}. These parameters agree well with those reported for this complex previously.[38] Similar $g_{\mathrm{av.}}$ and $A_{\mathrm{av.}}$ values have been reported for $[\mathrm{Cu(Hdpg)_2}]$.[38] Isotropic e.s.r. parameters for $[\mathrm{NiL''Cu(bipy)}][\mathrm{ClO_4}]_2$ were $g_{\mathrm{av.}} = 2.123$ and $A_{\mathrm{av.}} = 71 \times 10^{-4}$ cm^{-1}. From the parameters for the trinuclear and the reference complexes we may conclude that the unpaired electron of the trinuclear complexes is mostly localized on the terminal copper. This conclusion seems reasonable in view of the electronic structure of the spin-doublet ground state, $S_{\mathrm{T}} = \frac{1}{2}$ ($S_{23} = 1$), *i.e* $\mathrm{Cu}^2(\uparrow)$–$\mathrm{Cu}^1(\downarrow)$–$\mathrm{Cu}^3(\uparrow)$.

A quite different spectral feature was observed when the e.s.r. spectra were measured on frozen dmf solutions at liquid-nitrogen temperature. The complexes with bipy as the end-cap ligand, (**1**), (**2**), (**4**), and (**5**), showed axial e.s.r. spectra and each $g_{\parallel}$ component showed a well resolved seven-line hyperfine structure [Figure 7(*a*)]. In addition, the so-called 'half-field band' was observed around 1 600 G ($g \approx 4.2$). The observation of this band strongly suggests that the hyperfine structure arises from a spin-triplet species. The hyperfine coupling constant observed, (98—100) $\times 10^{-4}$ cm^{-1}, is about one half of that of common mononuclear copper(II) complexes of axial symmetry and is comparable to those of the spin-triplet states of magnetically coupled dicopper(II,II) complexes.[39—41] Since each trinuclear cation has one unpaired electron ($S = \frac{1}{2}$), its dimeric form stacked in the out-of-plane mode like $[\{\mathrm{Cu(Hdmg)_2}\}_2]$[19] is a candidate for the triplet species.

The e.s.r. spectrum of complex (**3**) possessing phen as the end-cap ligand was rhombic and its g_z component did not show a seven-line hyperfine structure. However, this complex also showed a prominent half-field band at $g = 4.19$, suggesting that it exists as a dimeric species in frozen solution.

The e.s.r. spectra of frozen methanol solutions resembled those of frozen dmf solutions but the hyperfine structure of the $g_{\parallel}$ component was poorly resolved [see Figure 7(*b*)]. From the spectral feature of the $g_{\parallel}$ component we presume that both the monomeric and dimeric species are coexisting in this case and the complexity of the $g_{\parallel}$ component results from superposition of a four-line (of the monomeric species) and a seven-line (of the dimeric species) hyperfine structure. In accord with this the half-field band observed was weak.

In view of the above facts we have re-examined the 1 300—1 800 G region of the e.s.r. spectra in dmf and methanol solutions at room temperature. Each complex exhibited a significant half-field band near $g = 4.2$ in dmf, though much weaker compared with that in frozen dmf solutions [see the insert of Figure 6(*b*)]. Evidently, appreciable amounts of the dimeric species exist in dmf and this may be the reason why the hyperfine structures of the $g \approx 2$ signal are not resolved. The half-field band was also noticed in methanol solutions, but the intensity of the signal was very weak in this case [see the insert of Figure 6(*c*)], suggesting that the amount of the dimeric species is negligibly small in this solvent.

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