Crystal Structures and Magnetism of Binuclear Copper(II) Complexes with Alkoxide Bridges. Importance of Orbital Complementarity in Spin Coupling through Two Different Bridging Groups†

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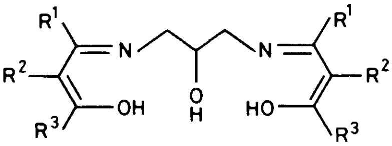
Binuclear copper(II) complexes, $[Cu_2(L^1)(O_2CMe)]\cdot H_2O$ (**1**), $[Cu_2(L^5)(O_2CMe)]\cdot MeOH$ (**2**), $[Cu_2(L^5)(O_2CPh)]\cdot H_2O$ (**3**), $[Cu_2(L^3)(O_2CMe)]$ (**4**), $[Cu_2(L^2)(O_2CMe)]$ (**5**), and $[Cu_2(L^4)(OMe)(MeOH)]$ (**6**) were prepared, where the ligands H_3L^n are 1 : 2 Schiff bases derived from 1,3-diaminopropan-2-ol and the carbonyl compounds acetylacetone (for L^1), benzoylacetone (for L^2), 3-ethoxymethylenepentane-2,4-dione (for L^3), methyl acetoacetate (for L^4), and salicylaldehyde (for L^5). The crystal structures of (**1**)—(**4**) and (**6**) were determined by *X*-ray analysis. The results revealed that all the complexes are binuclear and bridged by alkoxide and carboxylate oxygens except for (**6**) in which the exogenous bridging group comprises two hydrogen-bridged methoxide ions. In all complexes co-ordination geometries are essentially planar, and the angle formed by the two co-ordination planes falls in the range 5—19° for (**1**)—(**3**) and (**6**), whereas the angle in (**4**) is 54.6° indicating a large distortion from a coplanar structure. Antiferromagnetic coupling is strong for (**6**) ($-2J = 635\ cm^{-1}$) as expected from its large Cu–O–Cu angle (137.7°). However, the other complexes showed much lower antiferromagnetism though their Cu–O–Cu angles differ little from that of (**6**). The low antiferromagnetism of (**1**)—(**5**) was rationalised in terms of countercomplementarity of the orbitals between two bridging groups which participate in the superexchange interaction.

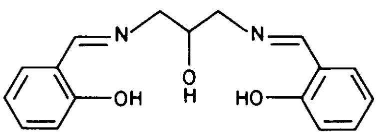
It has been revealed that spin coupling between copper(II) ions in di-μ-hydroxo-dicopper(II) complexes is deeply dependent on the Cu–O–Cu angle. According to Hodgson,[1] antiferromagnetic interaction becomes stronger with increasing Cu–O–Cu angle. The experimental data, including di-μ-alkoxo-dicopper(II) complexes so far reported, generally fall in line with this rule in the range of Cu–O–Cu angle 94—105°.[2] The quantum mechanical ground for this rule was given by Hoffmann[3] and other workers[4,5] in terms of a super-exchange mechanism.

Recently McKee and Smith[6] prepared a binuclear complex in which two copper(II) ions were linked by a single alkoxide oxygen with a larger Cu–O–Cu angle (135.5°).[6] Its magnetic moment ($\mu_{eff.} = 0.6$) at room temperature suggested that Hodgson's rule is applicable to the region of larger angle (~135°). This was also supported by the work on the mono-μ-hydroxo-dicopper(II) complexes with large Cu–O–Cu angle.[7,8] In the previous communication Nishida *et al.*[9] reported the preparation and structural characterization of a binuclear copper(II) complex $[Cu_2(L^1)(O_2CMe)]$ (1) (Figure 1) in which the copper ions are linked by alkoxide and acetate oxygens. The antiferromagnetic interaction of this complex is very weak ($\mu_{eff.} = 1.64$ at 295 K) in relation to its Cu–O–Cu angle (133.3°). It is apparent that a carboxylate bridge can also conduct an antiferromagnetic interaction as was verified in copper acetate and analogous compounds.[10–14] Accordingly, this result seemed to contradict to Hodgson's rule, and if so, Hoffmann's theory should be re-examined.

Thus, in this study we have prepared a series of binuclear complexes, $[Cu_2(L^5)(O_2CMe)]\cdot MeOH$ (2), $[Cu_2(L^5)(O_2CPh)]\cdot H_2O$ (3), $[Cu_2(L^3)(O_2CMe)]$ (4), $[Cu_2(L^2)(O_2CMe)]$ (5), and $[Cu_2(L^4)(OMe)(MeOH)]$ (6), and determined the crystal structures of (1)—(4) and (6) by *X*-ray diffraction [for compound (5), we could not obtain crystals suitable for *X*-ray analysis]. Based on the results, we have investigated the correlation between the magnetism and molecular structure in order to gain a comprehensive elucidation of magnetism of compounds of this kind. Part of this work was already reported by Nishida *et al.*[15]



	R^1	R^2	R^3
H_3L^1	Me	H	Me
H_3L^2	Me	H	Ph
H_3L^3	H	COMe	Me
H_3L^4	Me	H	OMe



H_3L^5

Experimental

Preparation of Ligands.—The Schiff-base ligands H_3L^n (n = 1—5) were prepared by the reaction of 1,3-diaminopropan-2-ol with acetylacetone, benzoylacetone, 3-ethoxymethylene-pentane-2,4-dione, methyl acetoacetate, and salicylaldehyde, respectively. The procedures are exemplified by that for H_3L^1.

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table 1. Crystal data for complexes **(1)**—**(4)** and **(6)**[a]

Complex	**(1)**	**(2)**	**(3)**	**(4)**[b]	**(6)**
Formula	$C_{15}H_{24}Cu_2N_2O_6$	$C_{20}H_{22}Cu_2N_2O_6$	$C_{24}H_{22}Cu_2N_2O_6$	$C_{17}H_{22}Cu_2N_2O_7$	$C_{15}H_{26}Cu_2N_2O_7$
M	455.5	513.5	561.5	493.5	469.4
Space group	$P2_1/n$	$Pbca$	$P2_1/c$	$P\bar{1}$	$P2_1/a$
a/Å	17.716(3)	18.196(5)	18.234(2)	13.398(8)	28.45(1)
b/Å	13.143(3)	22.636(5)	11.478(2)	16.024(5)	6.952(4)
c/Å	7.716(1)	9.731(1)	10.327(1)	11.691(3)	10.128(8)
α/°	90	90	90	111.92(2)	90
β/°	92.91(1)	90	100.09(1)	116.50(2)	110.96(4)
γ/°	90	90	90	64.09(3)	90
U/Å^3	1 794	4 008	2 128	2 016	1 871
Z	4	8	4	2	4
F(000)	936	2 046	1 144	1 008	968
D_c/g cm^{-3}	1.69	1.70	1.75	1.63	1.67
μ(Mo-K_α)/cm^{-1}	24.0	22.7	20.4	21.5	23.1
Crystal dimensions (mm)	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.5	0.3 × 0.4 × 0.5
Scan rate (° min^{-1})	6	6	6	6	6
Scan range (2θ/°)	3—55	3—55	3—55	3—55	3—55
Reflections collected	3 131	3 451	4 364	4 421	3 973
Independent reflections ($>3\sigma\lvert F_o\rvert$)	2 331	2 651	2 960	3 284	2 403
$R(=\Sigma\Vert F_o\rvert - \lvert F_c\Vert/\Sigma\lvert F_o\rvert)$	0.054	0.097	0.064	0.044	0.082
$R'[=(\Sigma\Vert F_o\rvert - \lvert F_c\Vert^2/\Sigma\lvert F_o\rvert^2)^{\frac{1}{2}}]$	0.068	0.101	0.074	0.048	0.091

[a] Estimated standard deviations are given in parentheses here and in Tables 2—12. [b] There are two dimeric molecules in the asymmetric unit.

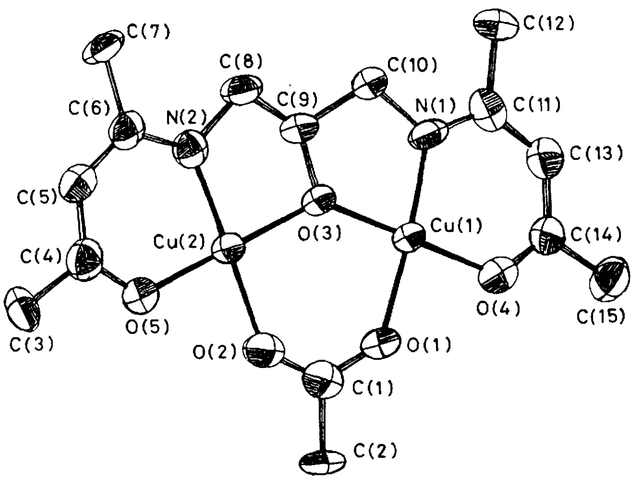

Figure 1. ORTEP drawing of $[Cu_2(L^1)(O_2CMe)]$ **(1)**

Acetylacetone and 1,3-diaminopropan-2-ol were mixed (2:1 mole ratio) in ethanol and refluxed for 2 h. The Schiff base was obtained as pale yellow crystals by distilling off the solvent.

Preparation of Metal Complexes.—The procedures are exemplified by that for $[Cu_2(L^1)(O_2CMe)]\cdot H_2O$ **(1)**. Copper(II) acetate monohydrate (400 mg, 2 mmol) was dissolved in hot methanol (20 cm^3). To this solution was added methanol–water (5:1, 25 cm^3) containing H_3L^1 (225 mg, 1 mmol) and triethylamine (300 mg, 3 mmol), and the mixture was left standing overnight. Greenish blue prisms separated which were filtered and desiccated over P_2O_5 (Found: C, 39.50; H, 5.30; N, 6.20. $C_{15}H_{24}Cu_2N_2O_6$ requires C, 39.55; H, 5.30; N, 6.15%). Complexes **(2)**—**(6)** were prepared by similar procedures to that above. In the case of **(3)**, copper(II) benzoate was used instead of copper(II) acetate. When H_3L^4 was used, the product incorporated no acetate ion in spite of applying the same procedure as that for **(1)**—**(5)**. Compound **(2)** (Found: C, 46.75; H, 4.40; N, 5.50. $C_{20}H_{22}Cu_2N_2O_6$ requires C, 46.80; H, 4.30; N, 5.45%). The methanol of crystallisation was removed by heating at 80 °C for 1 h under vacuum (Found: C, 47.40; H, 3.80; N, 5.80. $C_{19}H_{18}Cu_2N_2O_5$ requires C, 47.40; H, 3.75; N, 5.70%). Compound **(3)**: the water of crystallisation was removed by heating at 80 °C for 2 h (Found: C, 53.15; H, 3.70; N, 5.25. $C_{24}H_{20}Cu_2N_2O_5$ requires C, 53.05; H, 3.70; N, 5.15%). Compound **(4)** (Found: C, 41.25; H, 4.55; N, 5.75. $C_{17}H_{22}Cu_2N_2O_7$ requires C, 41.40; H, 4.50; N, 5.70%). Compound **(5)** (Found: C, 53.35; H, 4.65; N, 5.10. $C_{25}H_{26}Cu_2N_2O_5$ requires C, 53.45; H, 4.65; N, 5.00%). Compound **(6)** (Found: C, 38.10; H, 5.45; N, 5.90. $C_{15}H_{26}Cu_2N_2O_7$ requires C, 38.05; H, 5.55; N, 5.90%).

Measurements.—Magnetic susceptibilities were measured by the Faraday method over the temperature range 90—295 K. The instrument, equipped with a KAHN-200 electrobalance, was calibrated with $[Ni(NH_2CH_2CH_2NH_2)_3]S_2O_3$. Diamagnetic corrections were made by using Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{eff.} = (7.998\chi_A T)^{\frac{1}{2}}$, where χ_A represents the atomic magnetic susceptibility. Infrared spectra were obtained with a Hitachi 215 spectrophotometer on KBr pellets.

X-Ray Data Collection.—The crystals used for *X*-ray measurements were grown by slow evaporation from methanol solution. All measurements were made at 292 ± 1 K. The crystals were mounted on a Rigaku AFC-5 automatic diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Automatic centring and least-squares routines were carried out on 25 reflections for each complex to obtain the cell constants given in Table 1. The ω–2θ scan technique was employed to record the intensities for a unique set of reflections for which $3 < 2\theta < 55°$. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarisation effects.

Structure solution and refinement. In each case the positional parameters of the copper atoms were determined by direct methods.[16] The remaining non-hydrogen atoms were located

Table 2. Atomic co-ordinates ($\times 10^4$) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	4 262.7(6)	3 460.2(8)	1 358(1)	C(5)	5 857(6)	7 465(7)	5 064(13)
Cu(2)	4 742.4(6)	5 800.2(8)	3 283(1)	C(6)	6 205(5)	6 606(7)	4 328(12)
O(1)	3 349(4)	4 259(5)	1 601(9)	C(7)	7 067(5)	6 573(8)	4 465(14)
O(2)	3 662(4)	5 773(5)	2 817(9)	C(8)	6 208(5)	4 994(7)	2 839(12)
O(3)	4 911(3)	4 462(4)	2 409(8)	C(9)	5 647(5)	4 415(8)	1 679(13)
O(4)	3 611(4)	2 470(5)	283(9)	C(10)	5 850(5)	3 328(7)	1 350(13)
O(5)	4 587(4)	7 112(5)	4 215(8)	C(11)	5 207(6)	1 928(7)	−162(13)
N(1)	5 178(4)	2 787(6)	706(9)	C(12)	5 980(6)	1 471(8)	−488(15)
N(2)	5 812(4)	5 879(5)	3 510(9)	C(13)	4 558(6)	1 391(7)	−744(12)
C(1)	3 194(5)	5 149(7)	2 061(12)	C(14)	3 821(6)	1 686(7)	−560(12)
C(2)	2 395(5)	5 482(8)	1 689(15)	C(15)	3 197(5)	1 063(9)	−1 405(15)
C(3)	4 833(7)	8 688(7)	5 597(15)	O(6)	1 974(5)	2 958(9)	−20(15)
C(4)	5 107(6)	7 679(7)	4 933(13)				

Table 3. Atomic co-ordinates ($\times 10^4$) for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	711(1)	363.0(8)	3 811(2)	C(7)	−780(9)	1 746(7)	5 967(15)
Cu(2)	2 006(1)	−776.0(8)	3 688(2)	C(8)	−305(8)	1 359(7)	5 326(13)
O(1)	702(7)	16(4)	1 978(9)	C(9)	176(8)	1 026(6)	6 110(14)
O(2)	1 520(6)	−716(5)	1 943(9)	C(10)	1 117(9)	286(7)	6 616(14)
O(3)	1 431(5)	−157(4)	4 481(9)	C(11)	1 731(10)	51(7)	5 782(14)
O(4)	71(5)	933(5)	3 152(9)	C(12)	2 139(10)	−443(7)	6 466(15)
O(5)	2 629(5)	−1 338(4)	2 902(9)	C(13)	3 120(9)	−1 050(6)	5 639(15)
N(1)	616(7)	622(5)	5 692(11)	C(14)	3 495(9)	−1 427(7)	4 719(14)
N(2)	2 545(7)	−788(6)	5 413(10)	C(15)	4 144(12)	−1 686(8)	5 133(17)
C(1)	1 061(8)	−401(7)	1 434(12)	C(16)	4 575(12)	−2 090(9)	4 411(18)
C(2)	853(17)	−529(10)	−67(17)	C(17)	4 240(11)	−2 264(7)	3 143(17)
C(3)	−328(8)	1 304(6)	3 851(14)	C(18)	3 609(9)	−2 010(7)	2 693(16)
C(4)	−822(8)	1 676(7)	3 161(15)	C(19)	3 199(9)	−1 582(7)	3 394(14)
C(5)	−1 299(10)	2 054(7)	3 838(17)	O(6)	2 301(14)	6 485(12)	4 807(20)
C(6)	−1 286(10)	2 095(7)	5 294(17)	C(20)	2 861(16)	6 679(12)	4 225(20)

Table 4. Atomic co-ordinates ($\times 10^4$) for (3)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	3 467.3(6)	1 959.7(8)	8 056(1)	C(9)	2 757(8)	3 801(8)	6 600(12)
Cu(2)	2 040.2(7)	1 881.4(9)	5 332(1)	C(10)	2 228(7)	4 340(8)	5 593(11)
O(1)	3 184(4)	354(5)	7 669(7)	C(11)	1 375(5)	3 758(8)	3 651(8)
O(2)	2 174(4)	315(5)	6 077(6)	C(12)	946(5)	2 965(8)	2 757(8)
O(3)	2 742(4)	2 585(5)	6 659(5)	C(13)	504(6)	3 471(9)	1 621(9)
O(4)	4 182(4)	1 383(5)	9 447(6)	C(14)	58(6)	2 764(10)	707(9)
O(5)	1 342(4)	1 184(5)	3 934(5)	C(15)	31(6)	1 557(10)	911(10)
N(1)	3 619(4)	3 561(6)	8 551(7)	C(16)	459(6)	1 030(9)	2 020(9)
N(2)	1 827(4)	3 444(6)	4 703(7)	C(17)	940(5)	1 734(8)	2 955(8)
C(1)	4 584(5)	1 984(8)	10 398(8)	C(18)	2 598(5)	−104(6)	7 060(8)
C(2)	5 101(6)	1 366(8)	11 329(9)	C(19)	2 379(5)	−1 237(6)	7 539(7)
C(3)	5 514(6)	1 936(10)	12 388(9)	C(20)	2 826(5)	−1 761(8)	8 617(8)
C(4)	5 431(6)	3 156(10)	12 568(9)	C(21)	2 581(6)	−2 820(8)	9 090(9)
C(5)	4 947(6)	3 786(9)	11 659(9)	C(22)	1 915(7)	−3 340(8)	8 517(10)
C(6)	4 514(5)	3 214(8)	10 553(8)	C(23)	1 474(6)	−2 808(9)	7 451(10)
C(7)	4 037(6)	3 940(8)	9 624(9)	C(24)	1 719(5)	−1 755(8)	6 948(8)
C(8)	3 172(8)	4 389(8)	7 694(12)	O(6)	1 828(5)	3 270(8)	321(9)

by subsequent Fourier maps and least-squares refinement. The refinement was effected by the block-diagonal least-squares technique by using anisotropic thermal parameters. In the last stage of refinement, the difference Fourier map showed no significant peaks and all the parameter shifts were less than 0.4 σ. The final *R* values are listed in Table 1. Programs used for the structure solution and anisotropic refinement were supplied by the local version[17] of the UNICS system.[18] Atomic scattering factors were taken from ref. 19. All calculations were performed on a Facom M-200 computer at the Computer Center of Kyushu University. Final atomic co-ordinates are given in Tables 2—6.

Results and Discussion

Description of Structure of (**1**).—An ORTEP representation of the structure including the atomic numbering scheme is given in Figure 1. Selected bond distances and angles are listed in Table 7. The complex consists of binuclear molecules in which

Table 5. Atomic co-ordinates (× 10^4) for (**4**)

Atom	x	y	z	Atom	x	y	z
Cu(1)	5 657(1)	2 798.5(7)	1 555.7(9)	C(4)	7 115(12)	519(8)	4 017(11)
Cu(2)	4 224.7(9)	3 210.9(6)	−1 188.9(8)	C(5)	6 707(9)	1 250(6)	3 316(9)
O(1)	4 918(5)	4 164(4)	1 826(5)	C(6)	7 095(8)	998(6)	2 269(7)
O(2)	4 024(5)	4 482(3)	−127(5)	C(7)	7 270(8)	1 199(6)	484(7)
O(3)	5 781(5)	2 684(3)	−22(5)	C(8)	6 377(8)	1 727(6)	−594(8)
O(4)	5 533(6)	2 831(4)	3 087(6)	C(9)	5 446(8)	1 253(6)	−1 516(8)
O(5)	2 839(5)	3 693(3)	−2 579(4)	C(10)	3 989(8)	1 713(6)	−3 469(7)
O(15)	6 620(10)	574(6)	4 698(10)	C(11)	2 984(8)	2 305(5)	−4 261(7)
O(21)	1 590(5)	2 250(4)	−6 358(5)	C(12)	2 550(8)	1 877(6)	−5 601(7)
N(1)	6 743(6)	1 525(4)	1 487(6)	C(13)	3 339(9)	900(6)	−6 128(8)
N(2)	4 520(6)	1 972(4)	−2 261(6)	C(14)	2 427(8)	3 278(5)	−3 733(7)
C(1)	5 674(13)	2 510(8)	4 913(12)	C(15)	1 284(8)	3 894(6)	−4 518(8)
C(2)	5 956(9)	2 184(7)	3 694(9)	C(16)	4 092(9)	5 774(6)	1 685(8)
C(3)	8 187(13)	−349(9)	3 894(14)	C(17)	4 374(8)	4 718(5)	1 072(7)

Table 6. Atomic co-ordinates (× 10^4) for (**6**)

Atom	x	y	z	Atom	x	y	z
Cu(1)	6 814(1)	7 168(2)	1 871(1)	C(3)	9 671(7)	5 149(25)	6 402(19)
Cu(2)	8 186(1)	7 172(2)	3 243(1)	C(4)	9 235(5)	7 553(20)	4 673(14)
O(1)	7 058(4)	4 759(14)	2 770(13)	C(5)	9 272(5)	9 274(21)	4 033(14)
O(2)	7 944(4)	4 755(13)	3 648(10)	C(6)	8 843(5)	10 203(18)	3 010(12)
O(3)	7 496(3)	7 929(11)	2 091(8)	C(7)	8 956(5)	12 075(22)	2 417(16)
O(4)	6 145(3)	6 522(13)	1 775(10)	C(8)	7 972(4)	10 532(18)	1 545(15)
O(5)	8 856(3)	6 483(13)	4 477(10)	C(9)	7 498(5)	9 942(19)	1 833(16)
N(1)	6 610(4)	9 513(14)	817(11)	C(10)	7 023(4)	10 522(20)	594(15)
N(2)	8 396(3)	9 498(14)	2 644(11)	C(11)	6 045(5)	12 066(22)	−516(17)
O(6)	9 686(3)	6 930(15)	5 624(11)	C(12)	6 143(5)	10 207(18)	344(13)
O(7)	5 326(3)	6 928(15)	1 280(11)	C(13)	5 732(5)	9 290(20)	516(14)
C(1)	6 809(5)	3 629(23)	3 520(19)	C(14)	5 754(5)	7 583(20)	1 209(15)
C(2)	5 326(6)	3 621(23)	4 914(17)	C(15)	5 321(6)	5 185(26)	2 037(21)

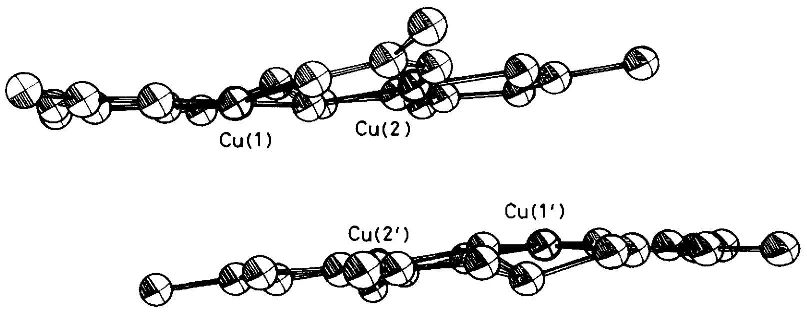

Figure 2. Stacking interaction between two molecules in (**1**) [Cu(2)–Cu(2′) 3.47, Cu(2)–Cu(1′) 4.18 Å]

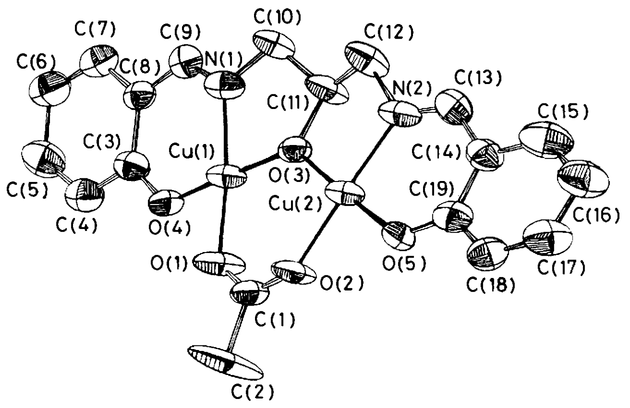

Figure 3. ORTEP drawing of [$Cu_2(L^5)(O_2CMe)$] (**2**)

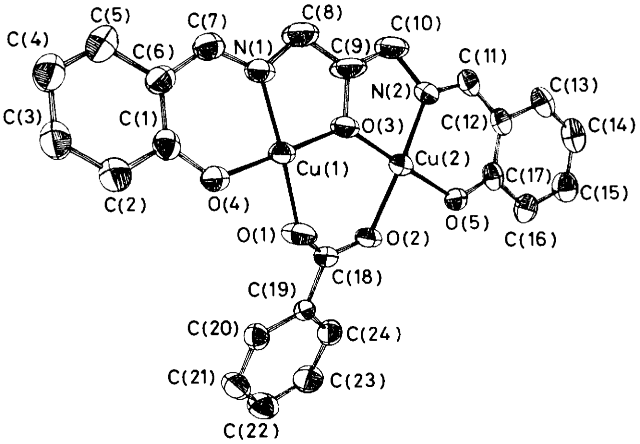

Figure 4. ORTEP drawing of [$Cu_2(L^5)(O_2CPh)$] (**3**)

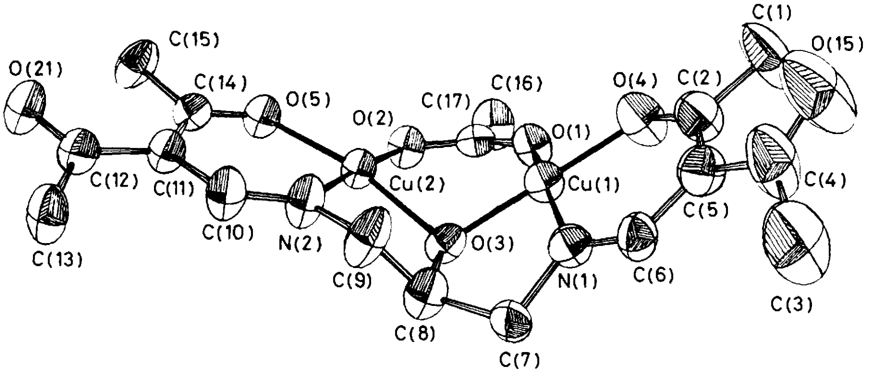

Figure 5. ORTEP drawing of $[Cu_2(L^3)(O_2CMe)]$ (4)

Table 7. Selected bond distances (Å) and angles (°) for (1)

Cu(1)–Cu(2)	3.502(2)	Cu(1)–O(1)	1.946(6)
Cu(1)–O(3)	1.902(6)	Cu(1)–N(1)	1.936(7)
Cu(1)–O(4)	1.903(6)	Cu(2)–O(2)	1.930(6)
Cu(2)–O(3)	1.913(6)	Cu(2)–N(2)	1.896(7)
Cu(2)–O(5)	1.893(6)	O(1)–C(1)	1.258(12)
O(2)–C(1)	1.285(11)	C(1)–C(2)	1.496(14)
O(5)–C(4)	1.288(12)	C(3)–C(4)	1.511(14)
C(4)–C(5)	1.357(15)	C(5)–C(6)	1.418(14)
C(6)–C(7)	1.526(14)	C(6)–N(2)	1.324(12)
N(2)–C(8)	1.467(12)	C(8)–C(9)	1.500(13)
C(9)–O(3)	1.441(11)	C(9)–C(10)	1.502(14)
C(10)–N(1)	1.454(12)	N(1)–C(11)	1.316(12)
C(11)–C(12)	1.528(15)	C(11)–C(13)	1.403(14)
C(13)–C(14)	1.377(14)	C(14)–C(15)	1.498(15)
O(4)–C(14)	1.283(12)		
Cu(1)–O(3)–Cu(2)	133.3(3)	O(1)–Cu(1)–O(4)	85.8(2)
O(1)–Cu(1)–O(3)	94.2(3)	O(1)–Cu(1)–N(1)	169.5(3)
O(3)–Cu(1)–N(1)	86.1(3)	O(3)–Cu(1)–O(4)	179.3(3)
O(4)–Cu(1)–N(1)	94.1(3)	O(2)–Cu(2)–O(5)	85.6(3)
O(2)–Cu(2)–N(2)	174.2(3)	O(2)–Cu(2)–O(3)	95.1(3)
O(5)–Cu(2)–N(2)	94.5(3)	O(3)–Cu(2)–N(2)	84.8(3)
O(3)–Cu(2)–O(5)	178.3(3)		

two copper atoms are linked by the alkoxide oxygen and acetate oxygens. Each copper ion is co-ordinated by one nitrogen and three oxygen atoms forming a co-ordination plane. The Cu–N and Cu–O bond distances are in the range of those of conventional Schiff-base and alkoxide-bridged copper(II) complexes of square-planar co-ordination.[2,20–24] The dihedral angle formed by the two co-ordination planes is 5.4°, thereby the whole molecule is nearly planar. Two molecules are partially stacked in the crystal as illustrated in Figure 2, where the shortest Cu–Cu distance is 3.47 Å. The interatomic distances between the stacked dimers are of the order of the van der Waals contact.

Molecular Structures of (2)—(4). Selected bond distances and angles for these complexes are listed in Tables 8—10. ORTEP diagrams are shown in Figures 3—5 for (2)—(4) respectively. Their structures are essentially the same as that of (1), having the alkoxide and carboxylate double-bridged structure. Co-planarity about copper atom and the dihedral angles formed by the two co-ordination planes of (2) and (3) also closely resemble those of (1). There are two dimeric molecules in the asymmetric unit for (4), and the structural data (which are very similar for both) for one of them are described in the text. The dihedral angle of the two co-ordination planes of (4) is large (54.6°), and hence the Cu–Cu separation (3.13 Å) and Cu–O–Cu angle (109°) are the smallest of these complexes. There is no stacking between molecules in crystals of (4) as was observed for (1)—(3).

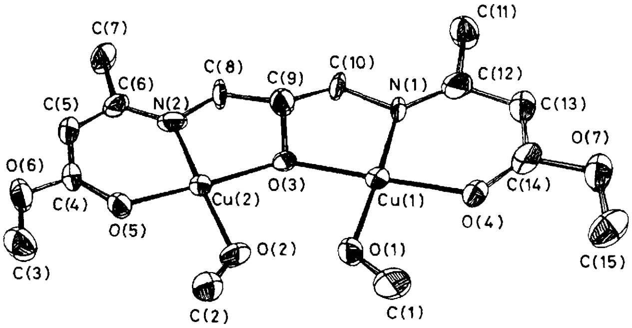

Figure 6. ORTEP drawing of $[Cu_2(L^4)(OMe)(MeOH)]$ (6)

Description of Structure of (6).—Selected bond distances and angles for (6) are listed in Table 11. The ORTEP drawing is shown in Figure 6. This compound incorporates no acetate group; instead there is strong hydrogen bonding between two co-ordinated methoxide oxygens, the O(1)–O(2) separation being 2.35 Å which is even shorter than the O–O distance in bis(dimethylglyoximato)nickel(II).[25] Thus, the two copper atoms are linked with an endogenous alkoxide bridge and an exogenous hydrogen-bonding system. Other structural features are similar to those of (1)—(4), though there is no stacking in (6).

Magnetic Properties.—The magnetic susceptibilities of (5) and (6) are shown as a function of temperature in Figure 7 as examples. These curves could be simulated by the equation based on the Heisenberg model, $\mathcal{H} = -2JS_1 \cdot S_2$, where $-2J$ corresponds to the energy separation between spin-singlet and -triplet states, by assuming the $-2J$ values given in Table 12 with $g = 2.10$ and $N\alpha = 60 \times 10^{-6}$ c.g.s. ($60/4\pi$ S.I.) units. The magnetic moment of (4) at room temperature is larger than the spin-only value, and obeys the Curie–Weiss law with $\theta = -24$ K.

The antiferromagnetic interaction in (1)—(5) is surprisingly smaller than that expected from their large Cu–O–Cu angles, as an extrapolation of di-μ-hydroxo-dicopper(II) complexes.[1,2] Although the dihedral angle between the two co-ordination planes seems to be related to the magnetic interaction, it cannot be the main factor in the reduction of the $-2J$ value because the decrease in the dihedral angle from 18.7 in (2) to 5.4° in (1)

Table 8. Selected bond distances (Å) and angles (°) for (**2**)

Cu(1)–Cu(2)	3.495(3)	Cu(1)–O(1)	1.950(9)
Cu(1)–O(3)	1.877(9)	Cu(1)–O(4)	1.852(10)
Cu(1)–N(1)	1.930(10)	Cu(2)–O(3)	1.912(9)
Cu(2)–O(2)	1.919(9)	Cu(2)–O(5)	1.868(10)
Cu(2)–N(2)	1.945(9)	C(1)–O(1)	1.265(19)
C(1)–O(2)	1.204(19)	C(1)–C(2)	1.537(22)
O(4)–C(3)	1.301(17)	C(3)–C(4)	1.404(22)
C(4)–C(5)	1.387(23)	C(5)–C(6)	1.420(23)
C(6)–C(7)	1.378(24)	C(7)–C(8)	1.380(21)
C(3)–C(8)	1.442(19)	C(8)–C(9)	1.384(20)
C(9)–N(1)	1.282(18)	N(1)–C(10)	1.489(19)
C(10–C(11)	1.480(23)	C(11)–O(3)	1.458(17)
C(11)–C(12)	1.498(24)	C(12)–N(2)	1.486(20)
N(2)–C(13)	1.222(21)	C(13)–C(14)	1.412(22)
C(14)–C(15)	1.380(26)	C(15)–C(16)	1.394(27)
C(16)–C(17)	1.431(25)	C(17)–C(18)	1.357(25)
C(18)–C(19)	1.399(22)	C(19)–O(5)	1.269(19)
C(14)–C(19)	1.441(20)		
Cu(1)–O(3)–Cu(2)	134.5(4)	O(1)–Cu(1)–O(3)	94.0(4)
O(1)–Cu(1)–N(1)	171.8(5)	O(1)–Cu(1)–O(4)	87.7(4)
O(3)–Cu(1)–N(1)	85.6(4)	O(4)–Cu(1)–O(1)	174.4(4)
N(1)–Cu(1)–O(4)	93.5(4)	O(2)–Cu(2)–O(5)	88.0(4)
O(2)–Cu(2)–N(2)	175.8(5)	O(2)–Cu(2)–O(3)	93.0(4)
O(5)–Cu(2)–N(2)	92.2(4)	O(5)–Cu(2)–O(3)	175.5(4)
N(2)–Cu(2)–O(3)	86.5(4)		

Table 9. Selected bond distances (Å) and angles (°) for (**3**)

Cu(1)–Cu(2)	3.482(2)	Cu(1)–O(1)	1.936(6)
Cu(1)–O(4)	1.883(6)	Cu(1)–O(3)	1.917(6)
Cu(1)–N(1)	1.915(7)	Cu(2)–O(2)	1.953(6)
Cu(2)–O(5)	1.924(5)	Cu(2)–O(3)	1.884(6)
Cu(2)–N(2)	1.924(5)	O(4)–C(1)	1.314(10)
C(1)–C(2)	1.414(12)	C(2)–C(3)	1.379(13)
C(3)–C(4)	1.423(16)	C(4)–C(5)	1.376(14)
C(5)–C(6)	1.429(13)	C(6)–C(7)	1.443(12)
C(7)–N(1)	1.305(11)	N(1)–C(8)	1.449(13)
C(8)–C(9)	1.416(16)	C(9)–O(3)	1.397(10)
C(9)–C(10)	1.429(16)	C(10)–N(2)	1.484(12)
N(2)–C(11)	1.294(11)	C(11)–C(12)	1.428(12)
C(12)–C(13)	1.425(12)	C(13)–C(14)	1.394(14)
C(14)–C(15)	1.394(14)	C(15)–C(16)	1.404(16)
C(16)–C(17)	1.404(13)	C(12)–C(17)	1.428(13)
C(1)–C(6)	1.430(12)	C(17)–O(5)	1.303(10)
O(1)–C(18)	1.256(10)	O(2)–C(18)	1.259(10)
C(19)–C(19)	1.471(11)	C(19–C(20)	1.395(11)
C(20)–C(21)	1.411(14)	C(21)–C(22)	1.390(15)
C(22)–C(23)	1.386(14)	C(23)–C(24)	1.417(14)
C(19)–C(24)	1.385(12)		
Cu(1)–O(3)–Cu(2)	132.7(3)	O(1)–Cu(1)–O(4)	86.9(2)
O(1)–Cu(1)–N(1)	171.6(3)	O(1)–Cu(1)–O(3)	94.4(2)
O(4)–Cu(1)–N(1)	94.9(3)	O(4)–Cu(1)–O(3)	178.6(2)
N(1)–Cu(1)–O(3)	83.7(3)	O(2)–Cu(2)–O(5)	86.2(2)
O(2)–Cu(2)–N(2)	174.1(3)	O(2)–Cu(2)–O(3)	94.9(2)
O(5)–Cu(2)–N(2)	93.8(3)	O(5)–Cu(2)–O(3)	178.1(3)
N(2)–Cu(2)–O(3)	85.3(3)		

Table 10. Selected bond distances (Å) and angles (°) for (**4**)

Cu(1)–Cu(2)	3.129(2)	Cu(1)–O(1)	1.935(5)
Cu(1)–O(4)	1.891(9)	Cu(1)–N(1)	1.916(6)
Cu(1)–O(3)	1.903(7)	Cu(2)–O(3)	1.938(5)
Cu(2)–O(2)	1.931(6)	Cu(2)–O(5)	1.939(4)
Cu(2)–N(2)	1.900(6)	O(4)–C(2)	1.266(14)
C(1)–C(2)	1.533(20)	C(2)–C(5)	1.429(11)
C(4)–C(5)	1.463(19)	C(4)–O(15)	1.220(24)
C(3)–C(4)	1.520(17)	C(5)–C(6)	1.423(17)
C(6)–N(1)	1.288(13)	N(1)–C(7)	1.475(14)
C(7)–C(8)	1.538(11)	C(8)–O(3)	1.446(8)
C(8)–C(9)	1.524(14)	C(9)–N(2)	1.481(10)
N(2)–C(10)	1.287(9)	C(10)–C(11)	1.428(10)
O(5)–C(14)	1.268(8)	C(11)–C(14)	1.428(10)
C(12)–C(13)	1.542(11)	C(12)–O(21)	1.235(9)
C(14)–C(15)	1.513(10)	O(1)–C(17)	1.256(11)
O(2)–C(17)	1.253(9)	C(16)–C(17)	1.518(11)
Cu(1)–O(3)–Cu(2)	109.1(3)	O(1)–Cu(1)–O(4)	89.7(3)
O(1)–Cu(1)–N(1)	165.7(3)	O(1)–Cu(1)–O(3)	93.6(2)
O(4)–Cu(1)–N(1)	91.9(3)	O(4)–Cu(1)–O(3)	176.4(3)
N(1)–Cu(1)–O(3)	85.4(3)	O(2)–Cu(2)–O(5)	90.5(2)
O(2)–Cu(2)–N(2)	175.3(4)	O(2)–Cu(2)–O(3)	93.4(2)
O(5)–Cu(2)–N(2)	90.4(2)	O(5)–Cu(2)–O(3)	168.4(3)
O(3)–Cu(2)–N(2)	84.8(2)		

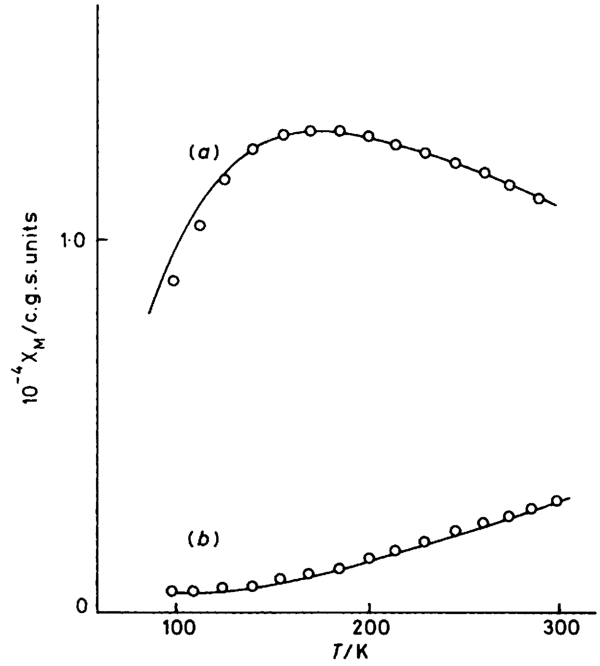

Figure 7. Variation with temperature of the molar susceptibility (per Cu^{II}) of (*a*) $[Cu_2(L^2)(O_2CMe)]$ (**5**) and (*b*) $[Cu_2(L^4)(OMe)(MeOH)]$ (**6**). (O) Experimental points; calculated from Bleaney-Bowers equation for values of parameters $-2J = 190$ cm^{-1}, $g = 2.10$, $N\alpha = 60 \times 10^{-6}$ c.g.s. units for (**5**) and $-2J = 635$ cm^{-1}, $g = 2.10$, $N\alpha = 60 \times 10^{-6}$ c.g.s. units for (**6**) [χ_M (c.g.s.) $= \frac{10^6}{4\pi}\chi_M$ (S.I.)]

does not bring about a significant increase in $-2J$ value, as seen in Table 12.

In contrast to these results, a much larger antiferromagnetic interaction is operating in (**6**), similar to that in the complex of McKee and Smith,[6] and in accordance with that expected from its large Cu–O–Cu angle (137.7°). Since the difference between (**6**) and (**1**)—(**5**) is obviously the absence of a carboxylate bridge in (**6**), the reduction of the antiferromagnetic interaction must be caused by the carboxylate bridge, although this bridge itself conducts an antiferromagnetic interaction as verified in many copper(II) carboxylates.[10–14] In order to gain a reasonable explanation for these facts we have examined the superexchange mechanism of this system in terms of Hoffmann's theory.[3]

In planar copper(II) complexes, an unpaired electron resides in a d_{xy} orbital, and the symmetric and antisymmetric combinations of these orbitals are expressed as in equations (1) and (2) (for the definition of x and y co-ordinates, see Figure 8).

$$\varphi_a = d_{xy} + d_{xy}' \tag{1}$$

$$\varphi_s = d_{xy} - d_{xy}' \tag{2}$$

According to Hoffmann and co-workers,[3] in a bimetallic system the larger the energy separation between the symmetric (φ_a) and antisymmetric (φ_s) combinations of the two magnetic orbitals, the stronger is the antiferromagnetic interaction, irrespective of which combination of the orbitals is lower in energy. On this basis, spin exchange interaction of hydroxide- or alkoxide-bridged binuclear copper(II) complexes can be reasonably explained in the following manner. In such a system the oxygen p_x orbital interacts with φ_a to raise its energy, whereas it is orthogonal to the φ_s orbital and exerts no effect on it (see Figure 8). On the other hand, the effects of p_y on φ_a and φ_s are reversed, *i.e.*, raising φ_s but not φ_a. When the Cu–O–Cu angle is larger than 90°, the effect of p_x on the magnetic orbitals exceeds that of p_y so that the larger energy separation of φ_s and φ_a brings about a stronger antiferromagnetic interaction.[3]

In the case of the acetate bridge the separation of φ_s and φ_a is effected by the highest occupied molecular orbital (h.o.m.o.) of the acetate ion as shown in Figure 8,[3,26] where the energy of φ_s is lifted and that of φ_a left unaltered. Therefore, when the copper(II) ions are linked by alkoxide oxygen and acetate ion as is the present case, the energies of φ_s and φ_a are lifted by the acetate and alkoxide bridges, respectively, resulting in the diminished energy separation of φ_a and φ_s compared with that of a single-alkoxide-bridged complex. Thus, the reduced antiferromagnetism of the complexes **(1)**—**(4)** is reasonably explained.

It should be emphasized that in a binuclear complex with two different bridging groups (which will be denoted as heterobridged binuclear complexes), the bridging groups act complementarily or countercomplementarily in inducing antiferromagnetic interaction depending on the symmetries of their h.o.m.o.s which interact with magnetic orbitals.[3,5,15] Accordingly, the bridging groups in the heterobridged binuclear complexes containing an alkoxide bridge as studied here can be

Table 11. Selected bond distances (Å) and angles (°) for **(6)**

Cu(1)–Cu(2)	3.644(2)	Cu(1)–O(3)	1.944(9)
Cu(1)–O(1)	1.914(13)	Cu(1)–O(4)	1.923(9)
Cu(1)–N(1)	1.920(9)	Cu(2)–O(3)	1.964(9)
Cu(2)–N(2)	1.897(10)	Cu(2)–O(5)	1.930(10)
Cu(2)–O(2)	1.915(9)	O(1)–C(2)	1.442(24)
O(4)–C(14)	1.286(18)	C(14)–O(7)	1.327(19)
O(7)–C(15)	1.427(24)	C(13)–C(14)	1.369(21)
C(13)–C(12)	1.394(20)	C(12)–C(11)	1.527(21)
C(12)–N(1)	1.331(19)	N(1)–C(10)	1.452(20)
C(10)–C(9)	1.533(21)	C(9)–O(3)	1.424(19)
C(8)–C(9)	1.533(22)	N(2)–C(8)	1.501(18)
N(2)–C(6)	1.287(18)	C(6)–C(7)	1.516(22)
C(6)–C(5)	1.441(21)	C(5)–C(4)	1.382(21)
C(4)–O(5)	1.265(21)	C(4)–O(6)	1.370(18)
C(3)–O(6)	1.476(22)	O(2)–C(1)	1.450(21)

Cu(1)–O(3)–Cu(2)	137.7(5)	O(1)–Cu(1)–O(4)	90.2(5)
O(1)–Cu(1)–N(1)	173.2(5)	O(1)–Cu(1)–O(3)	90.4(4)
O(4)–Cu(1)–N(1)	94.2(5)	O(4)–Cu(1)–O(3)	175.9(4)
O(3)–Cu(1)–N(1)	85.6(4)	O(2)–Cu(2)–O(3)	90.2(4)
O(2)–Cu(2)–N(2)	174.2(5)	O(2)–Cu(2)–O(5)	89.5(4)
O(3)–Cu(2)–N(2)	86.8(4)	O(3)–Cu(2)–O(5)	176.5(4)
N(2)–Cu(2)–O(5)	93.9(4)		

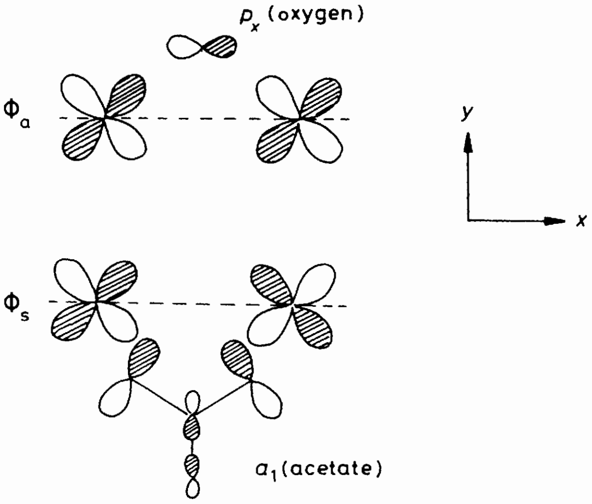

Figure 8. Symmetric (φ_a) and antisymmetric (φ_s) combinations of metal *d* orbitals

Table 12. Magnetic and structural data[a]

Complex	**(1)**	**(2)**	**(3)**	**(4)**	**(6)**
$\mu_{eff.}$ (295 K)	1.64	1.63	1.65	1.77	0.74
$-2J$/cm^{-1}	165	170	160	$\theta = -24$ K[b]	635
Cu(1)–O(3)–Cu(2)/°	133.3(3)	134.5(5)	132.7(3)	109.1(3)	137.7(5)
Cu(1)–Cu(2)/Å	3.502(2)	3.495(3)	3.482(2)	3.129(2)	3.644(2)
Cu(1)–O(3)/Å	1.902(6)	1.877(9)	1.917(6)	1.903(7)	1.944(9)
Cu(2)–O(3)/Å	1.913(6)	1.912(9)	1.884(6)	1.938(5)	1.964(9)
O(1)–O(2)/Å	2.258(9)	2.226(17)	2.243(8)	2.234(8)	2.354(16)
τ[c]/°	5.4	18.7	8.2	54.6	15.3
d[d] Cu(1)	−0.017	0.010	0.027	−0.300	0.080
d[d] Cu(2)	−0.007	0.024	−0.088	−0.399	0.085
d[d] O(1)	0.011	−0.024	0.044	0.038	−0.026
d[d] O(2)	−0.004	0.006	−0.081	0.158	−0.018
d[d] O(3)	0.017	−0.016	0.098	0.502	−0.120
d[d] C*[e]	−0.67	0.30	0.14	0.54	0.22
Solid angle around O(3)/°[f]	352.8	358.1	360	334.9	353.8

[a] See Figures 2—7 for the atomic numbering system. [b] Magnetic properties were elucidated in terms of the Curie–Weiss law, $\chi = C/(T - \theta)$. [c] Dihedral angle (°) between co-ordination planes, Cu(1)N(1)O(1)O(4) and Cu(2)N(2)O(2)O(3)O(5). [d] Deviations (Å) from the best plane Cu(1)Cu(2)O(1)O(2)O(3). [e] Carbon atom attached to the alkoxide-oxygen atom. [f] Summation of the angles Cu(1)–O(3)–Cu(2), Cu(1)–O(3)–C*, and Cu(2)–O(3)–C*.

classified into two groups in terms of the symmetry of their h.o.m.o.s: *e.g.*, (A) bidentate carboxylate bridge which acts countercomplementarily,[15] and ligands of similar co-ordination mode such as dithiocarbamate, carbonate, and nitrite (*OO*-chelate), *etc.*, and (B) bidentate azide ion which acts complementarily.[15,27]

In the course of the preparation of this article Mazurek *et al.*[28] have reported the synthesis and magnetic properties of binuclear copper(II) complexes similar to ours. While they seemed to accept the orbital countercomplementary effect proposed by us as one of the factors for the spin coupling, they emphasised the effect of the bonding geometry of endogenous alkoxide oxygen. We have become aware that this effect is one of the most important factors for spin coupling in binuclear copper(II) complexes.[2,20,23,29–33] However, it is clearly shown in this paper that the countercomplementary effect dramatically alters antiferromagnetic coupling, since compound (**6**) shows much stronger antiferromagnetism than the other complexes in spite of the fact that the planarity about the endogenous bridging oxygen of (**6**) is no better than those of other complexes (see Table 12).

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