The structural determination of Ph_3GeOH is part of a series for the Group 14 Ph_3MOH molecules (M = C, Si, Ge, Sn, Pb). Crystals of Ph_3COH (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992) are trigonal, $R\bar{3}$, with 1.33 molecules in the asymmetric unit and consist of hydrogen-bonded pyramidal tetramers with one molecule on a threefold axis and the other three lying around it. The Ph_3SiOH structure is isomorphous with Ph_3GeOH. Both Ph_3SnOH and Ph_3PbOH have structures consisting of zigzag chains of planar Ph_3M (M = Sn, Pb) groups joined by OH groups giving trigonal bipyramidal geometry at M (Glidewell & Liles, 1978*b*).

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Structure of *catena*-Poly[{(2,2′-bipyridyl)(diperchlorato)copper(II)}-μ-4,4′-bipyridyl]

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Abstract. $[Cu(C_{10}H_8N_2)(C_{10}H_8N_2)(ClO_4)_2]$, M_r = 574.5, orthorhombic, *Pbcn*, a = 12.413 (3), b = 14.645 (3), c = 12.287 (2) Å, V = 2233.6 (8) Å^3, Z = 4, D_x = 1.708 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 13.12 cm^{-1}, $F(000)$ = 1164, room temperature, R = 0.050 and wR = 0.049 for 1498 observed reflections. The coordination around Cu^{II} is an elongated distorted octahedron. Two N atoms of 2,2′-bipyridyl and two N atoms from two 4,4′-bipyridyls form the equatorial coordination plane, and two perchlorate ions occupy the axial sites. The 4,4′-bipyridyl ligand bridges neighbouring Cu^{II} atoms to form polymeric chains along the c axis in the crystal. The rings of 4,4′-bipyridyl are coplanar and make a dihedral angle of 114° with the equatorial coordination plane; the 4,4′-bipyridyl may provide a pathway for magnetic superexchange interaction between the adjacent Cu^{II} atoms.

Introduction. In the last decade, a number of binuclear transition-metal complexes bridged by heterocyclic aromatic diamines have been investigated as models of metalloenzymes (Matsumoto, Ooi, Nakao, Mori & Nakahara, 1981; Richardson & Hatfield, 1975). In some imidazolate or pyrazine-bridged complexes, spin–spin exchange interactions, propagated by the bridging ligand between the adjacent metal ions, have been observed, and studies on the molecular and crystal structures of those complexes have shown the relationship between structure and magnetic property (Coronado, Drillon & Beltran, 1984; Xu, Chen, Xu, Cheng, Chen & Tang, 1991). Recently, a series of novel Cu^{II} complexes bridged by 4,4′-bipyridyl ligands have been synthesized, and studies on EPR spectra showed evidence of superexchange interaction propagated by the 4,4′-bipyridyl ligand in the title complex, but no interaction in the others (Chen, 1989). In order to investigate the structural reason for the differences in the magnetic properties, the crystal structures of these complexes have been determined by means of X-ray analysis.

Experimental. 2,2′-Bipyridyl (2 mmol) and 4,4′-bipyridyl (2 mmol) were dissolved in ethanol, and then the solution was mixed with an aqueous solu-

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tion containing 2 mmol $Cu(ClO_4)_2$. The mixture was refluxed for 4 h. Dark blue crystals were grown by slow evaporation at room temperature. Crystal dimensions 0.35 × 0.40 × 0.40 mm; Enraf–Nonius CAD-4 diffractometer; unit-cell parameters by 25 reflections ($20 \leq 2\theta \leq 32°$); graphite-monochromated Mo $K\alpha$ radiation; ω–2θ scan, variable scan rate 1–4° min^{-1}, scan width $\Delta\omega = (0.65 + 0.35\tan\theta)°$. 2254 independent reflections (2θ up to 50°, $h = 0$ to 14, $k = 0$ to 17, $l = 0$ to 14), 1498 observed reflections [$|F_o| \geq 3\sigma(F_o)$]; three standard reflections showed no intensity variation; Lp correction; no absorption or extinction corrections. Structure solved by Patterson method followed by Fourier syntheses; block-diagonal least squares using a modified version of *HBLS*-V (Miki, 1987); function $\sum w(|F_o| - |F_c|)^2$ minimized with unit-weighting scheme. H atoms placed 1.0 Å from bonded C atoms. Refinement with anisotropic thermal parameters for non-H atoms and with fixed isotropic thermal parameter $B = 4.0$ Å^2 for H atoms led to convergence with $(\Delta/\sigma)_{\max} = 0.13$ for non-H atoms. $R = 0.050$, $wR = 0.049$, $S = 3.68$, $\Delta\rho_{\max} = 0.7$ and $\Delta\rho_{\min} = -0.3$ e Å^{-3}. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations performed on a Honeywell DPS8/49 computer at The Computation Center of Zhejiang University.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *of non-*H *atoms, with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)].$$

	x	y	z	B_{eq}
Cu	0.0	0.19151 (5)	0.25	3.16
Cl	0.2977 (1)	0.1870 (1)	0.1991 (1)	4.4
O(1)	0.1883 (4)	0.1834 (5)	0.1749 (5)	9.4
O(2)	0.3391 (7)	0.1000 (4)	0.1954 (6)	11.1
O(3)	0.3466 (7)	0.2431 (5)	0.1281 (7)	12.2
O(4)	0.3000 (5)	0.2209 (4)	0.3094 (5)	9.5
N(1)	0.0524 (3)	0.0892 (3)	0.3428 (3)	3.0
N(2)	0.0279 (4)	0.2910 (3)	0.3600 (3)	3.6
C(1)	0.0358 (4)	0.0058 (3)	0.3018 (4)	3.5
C(2)	0.0801 (5)	−0.0729 (4)	0.3443 (5)	4.3
C(3)	0.1428 (5)	−0.0638 (4)	0.4352 (6)	4.4
C(4)	0.1589 (5)	0.0203 (4)	0.4815 (5)	4.4
C(5)	0.1125 (5)	0.0962 (4)	0.4324 (4)	3.8
C(6)	0.0890 (5)	0.3633 (4)	0.3333 (5)	4.2
C(7)	0.0798 (4)	0.4464 (3)	0.3865 (5)	3.9
C(8)	0.0072 (5)	0.4556 (3)	0.4723 (4)	3.1
C(9)	−0.0496 (5)	0.3782 (3)	0.5035 (5)	4.1
C(10)	−0.0372 (5)	0.2987 (3)	0.4449 (4)	4.1

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu—O(1)	2.516 (7)	Cu—N(1)	1.992 (4)
Cu—N(2)	2.017 (4)	N(1)—C(1)	1.337 (7)
N(1)—C(5)	1.334 (7)	N(2)—C(6)	1.343 (7)
N(2)—C(10)	1.324 (7)	C(1)—C(1*)	1.554 (11)
C(1)—C(2)	1.379 (8)	C(2)—C(3)	1.368 (9)
C(3)—C(4)	1.371 (9)	C(4)—C(5)	1.390 (9)
C(6)—C(7)	1.386 (8)	C(7)—C(8)	1.393 (8)
C(8)—C(81)	1.480 (1)	C(8)—C(9)	1.389 (8)
C(9)—C(10)	1.376 (9)	Cl—O(1)	1.390 (8)
Cl—O(2)	1.375 (8)	Cl—O(3)	1.344 (9)
Cl—O(4)	1.444 (6)		

O(1)—Cu—O(1*)	174.6 (2)	O(1)—Cu—N(1)	82.6 (2)
O(1)—Cu—N(1*)	93.3 (2)	O(1)—Cu—N(2)	96.9 (2)
O(1)—Cu—N(2*)	87.0 (2)	N(1)—Cu—N(1*)	82.4 (2)
N(1)—Cu—N(2*)	95.9 (2)	N(1)—Cu—N(2*)	169.4 (2)
N(2)—Cu—N(2*)	87.6 (2)	Cu—N(1)—C(5)	126.6 (4)
Cu—N(1)—C(1)	114.9 (3)	Cu—N(2)—C(6)	120.1 (4)
C(1)—N(1)—C(5)	117.9 (5)	C(6)—N(2)—C(10)	118.0 (5)
Cu—N(2)—C(10)	119.0 (4)	N(1)—C(1)—C(2)	124.1 (5)
N(1)—C(1)—C(1*)	113.4 (4)	C(1)—C(2)—C(3)	117.0 (6)
C(1*)—C(1)—C(2)	122.6 (5)	C(3)—C(4)—C(5)	118.6 (6)
C(2)—C(3)—C(4)	120.6 (6)	N(2)—C(6)—C(7)	122.0 (5)
N(1)—C(5)—C(4)	121.8 (5)	C(7)—C(8)—C(8†)	120.8 (5)
C(6)—C(7)—C(8)	119.7 (5)	C(8†)—C(8)—C(9)	122.0 (5)
C(7)—C(8)—C(9)	117.3 (5)	N(2)—C(10)—C(9)	123.5 (6)
C(8)—C(9)—C(10)	119.3 (6)	O(1)—Cl—O(3)	109.0 (5)
O(1)—Cl—O(2)	108.9 (5)	O(2)—Cl—O(3)	112.1 (5)
O(1)—Cl—O(4)	103.5 (4)	O(3)—Cl—O(4)	113.0 (5)
O(2)—Cl—O(4)	110.0 (4)		

Symmetry code: (*) $-x, y, 0.5 - z$; (†) $-x, -y, 1 - z$.

Discussion. The atomic coordinates and thermal parameters for non-H atoms are listed in Table 1.† Bond distances and angles are listed in Table 2. The Cu^{II} atom is located on a twofold axis. Two N atoms of a bidentate 2,2′-bipyridyl ligand *cis* coordinate to the Cu^{II} atom in the equatorial plane with Cu—N distances of 1.992 (4) Å, while two N atoms from two 4,4′-bipyridyl ligands occupy the other *cis* sites in the plane with Cu—N distances of 2.017 (4) Å. Two perchlorate groups in the axial direction semi-coordinate to the Cu^{II} atom with Cu—O distances of 2.516 (7) Å to complete six-coordination (see Fig. 1). The deviations of the ligating N atoms from their mean plane are from −0.25 to 0.21 Å and the dihedral angle between the N(1)CuN(1*) and N(2)CuN(2*) planes is 15.3°, both of which indicate a significant tetrahedral distortion of the square-planar coordination geometry in the equatorial plane. In the 2,2′-bipyridyl ligand the pyridine rings are twisted by 13.5° about the 2,2′-carbon bond, which is compared to the 13.9° found in $Cu(2,2'$-$bpy)_2(ClO_4)_2$ (Foley, Kennefick, Phelan, Tyagi & Hathaway, 1983). There are no abnormal bond lengths and angles in the 2,2′-bipyridyl ligand. The bridging ligand 4,4′-bipyridyl is located about a crystallographic centre of inversion, thus the pyridine rings are essentially coplanar, the atomic maximum deviation from the least-squares plane being 0.052 Å. This is comparable with that found in $[\{CuNH(CH_2COO)_2\}_2(C_{10}H_8N_2)]$ (Xu, Cheng, Xu & Zhou, 1987), but is in contrast with another Cu^{II} complex, in which the pyridine rings of the 4,4′-bipyridyl significantly twist about the 4,4′-carbon bond (Xu & Shi, 1986). The equatorial coordination

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54926 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0546]

planes of the neighbouring Cu^{II} atoms are nearly coplanar, the dihedral angle being only 0.5°.

It is notable that the 4,4′-bipyridyl plane is canted relative to the equatorial coordination planes with a dihedral angle of about 114°. As previously reported (Xu, Chen, Xu, Cheng, Chen & Tang, 1991), such a tilt seems to result from short contacts between the bridging ligand and the neighbouring ligating atoms; in the present complex the C(10)···O(1*) and C(6)···N(2*) distances are 2.922 (10) and 2.987 (7) Å, respectively. The X-band ESR spectrum of a powdered sample of the crystal shows evidence of magnetic superexchange interaction between the Cu^{II} atoms (Chen, 1989). According to the magnetic superexchange mechanism (Richardson & Hatfield, 1975) and the results of EHMO calculations (Cheng, 1988), the coplanar bridge ligand 4,4′-bipyridyl canted to the equatorial coordination plane may provide an π propagating pathway for magnetic superexchange interaction between the adjacent Cu^{II} atoms in the title complex.

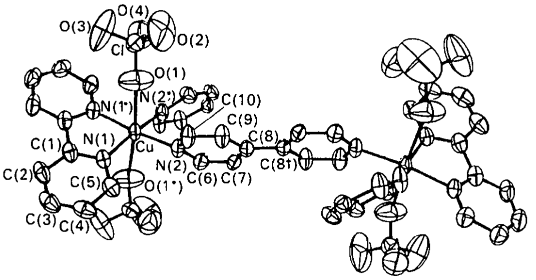

Fig. 1. Monomer molecular structure of the title compound together with the atomic numbering system. H atoms are omitted for clarity.

As illustrated in Fig. 2, the 4,4′-bipyridyl ligands bridge the neighbouring Cu^{II} atoms to form polymeric chains; thus the crystal structure consists of one-dimensional zigzag molecular chains along the *c* axis. There is no bonding interaction between the chains, the nearest distance being 3.298 Å [O(4)···C(9)(0.5 + x, 0.5 − y, z)].

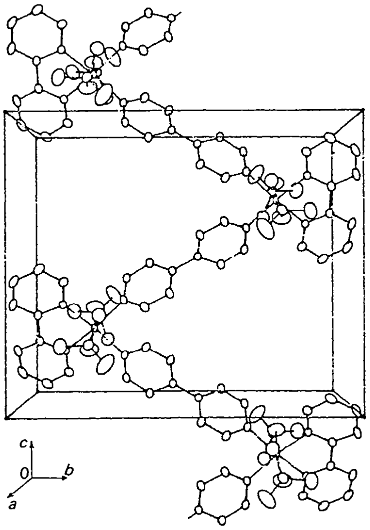

Fig. 2. Crystal structure of the title compound viewed along the *a* axis. H atoms are omitted for clarity.

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