

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

	$B_{\text{eq}} = (8\pi^2/3) \text{ trace } U.$			B_{eq}
	x	y	z	
K	0.0	0.0	0.25	2.20 (7)
In	0.0	0.5	0.25	1.41 (3)
Te	0.32456 (5)	0.17544*	0.0	1.39 (2)

$$* y = \frac{1}{2} - x.$$

Table 2. Important geometry (\AA , $^\circ$) for polyhedra in KInTe_2

KTe ₈ polyhedron	
K—Te ^{a,b,c,d,e,f,g,h}	3.6612 (7) (8×)
Te ^{a/c/e/g} —K—Te ^{b/d/f/h}	120.09 (2) (4×)
Te ^{a/b/e/f} —K—Te ^{c/d/g/h}	80.68 (2) (4×)
Te ^{a/b/c/d} —K—Te ^{e/f/g/h}	75.56 (1) (8×)
Te ^{a/b/e/f} —K—Te ^{d/c/h/g}	131.34 (2) (4×)
Te ^{a/b/c/d} —K—Te ^{g/h/f/e}	67.74 (2) (4×)
Te ^{a/b/c/d} —K—Te ^{h/g/e/f}	151.33 (2) (4×)
InTe ₄ polyhedron	
In—Te ^{e,g,i,j}	2.8094 (8) (4×)
Te ^{e/e/g/i} —In—Te ^{g/i/i/j}	115.05 (2) (4×)
Te ^{e/g} —In—Te ^{i/j}	98.81 (3) (2×)

Symmetry codes: (a) x, y, z ; (b) $-x, -y, z$; (c) $x, -y, \frac{1}{2} + z$; (d) $-x, y, \frac{1}{2} + z$; (e) $-y, x, z$; (f) $y, -x, z$; (g) $y, x, \frac{1}{2} + z$; (h) $-y, -x, \frac{1}{2} + z$; (i) $y, 1 - x, z$; (j) $-y, 1 - x, \frac{1}{2} + z$.

On the basis of the intensity statistics, as well as the successful solution and structure refinements, the space group was determined to be $I4/mcm$ (No. 140).

Data reduction: *TEXSAN PROCESS* (Molecular Structural Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. The atomic coordinates were found by direct methods using *SHELXS86* (Sheldrick, 1985).

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71217 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1049]

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Structure of Dimeric Dichloro(4,4'-dimethyl-2,2'-bipyridine)copper(II) Hemihydrate

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Abstract

The crystal consists of discrete dimeric units, di- μ -chloro-bis[chloro(4,4'-dimethyl-2,2'-bipyridine)copper(II)] hydrate, linked to one water molecule and to another unit by van der Waals forces. Each dimeric unit contains a Cu_2Cl_2 core surrounded by two chlorine ions and two 4,4'-dimethyl-2,2'-bipyridine ligands. The geometry about each Cu atom is best described as a distorted trigonal bipyramid. The basal plane contains the N(2) atom of 4,4'-dimethyl-2,2'-bipyridine, the Cl(2a) atom that bridges the two monomers, and the Cl(1) ion. The two axial sites are occupied by the N(1) atom and the Cl(2) ion.

Comment

The present work continues structural studies of Cu^{II} complexes with diimines. The dichloro(4,4'-dimethyl-2,2'-bipyridine)copper(II) complex has been

prepared and its structure determined in order to make a comparison with the structure of *catena*-poly[di- μ -chloro(2,2'-bipyridine)copper(II)] reported previously (Garland, Grandjean, Spodine, Atria & Manzur, 1988).

The reported dimeric complex has a Cu_2Cl_2 core with the two Cu atoms separated by 3.611 (1) Å. The two halves of the dimer are related by a crystallographic twofold axis. The Cu(1)—Cl(2)—Cu(1a)—Cl(2a) unit is planar, the atoms deviating from the least-squares plane by -0.1084 , $+0.1084$, -0.1084 and $+0.1084$ Å, respectively.

The geometry about each Cu atom could be described as a distorted trigonal bipyramid. The basal plane contains the N(2) atom, the bridging Cl(2a) ion and the Cl(1) ion, with the two axial sites occupied by the N(1) atom and the Cl(2) ion. This model is severely distorted with a dihedral angle, formed by the best mean planes Cl(1)—Cu(1)—N(1)—N(2) and Cl(1)—Cu(1)—Cl(2)—N(2), of 9.14° instead of the 60° characteristic of an idealized trigonal bipyramid.

This structure could alternatively be described as a distorted square pyramid consisting of the two *cis* N atoms from the organic molecule and the two *cis* Cl atoms, with the apical site occupied by the Cl atom from the other monomer unit.

The Cu(1), N(1), N(2), Cl(1) and Cl(2) atoms lie in the basal plane deviating from it by -0.1564 , -0.2911 , $+0.3664$, $+0.2927$ and -0.2117 Å, respectively, while the axial distance of Cl(2a) to the basal plane is -2.8822 Å.

The dihedral angle between the unweighted mean planes N(1)—Cu(1)—N(2) and Cl(1)—Cu(1)—Cl(2) is 27.5° , indicating a distortion towards tetrahedrality, which is quite common in '4 + 1' complexes.

If we compare this structure with the homologous *catena*-poly[di- μ -chloro(2,2'-bipyridine)copper(II)], which contains a non-methylated 2,2'-bipyridine ligand (Garland *et al.*, 1988), we find that the distances and angles of the organic ligands are comparable but the Cu_2Cl_2 units are quite different. In the *catena* compound the Cu_2Cl_2 core is planar due to an inversion center in the middle of the molecule, and

the dimeric units are linked to form a linear polymer, while the coordination around the copper is '4 + 2'. In the present case the dimeric units are linked by van der Waals forces.

These significant differences between the two complexes can be attributed to the presence of methyl groups in the 4,4'-dimethyl-2,2'-bipyridine ligand which, through steric effects, prevent the formation of a catenated structure.

Experimental

Crystal data

$[\text{CuCl}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)] \cdot 0.5\text{H}_2\text{O}$

$M_r = 327.7$

Monoclinic

$C2/c$

$a = 9.134$ (4) Å

$b = 16.801$ (6) Å

$c = 17.335$ (8) Å

$\beta = 99.15$ (3) $^\circ$

$V = 2626$ (2) Å³

$Z = 8$

$D_x = 1.657$ Mg m⁻³

Mo K α radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 5$ – 20°

$\mu = 2.052$ mm⁻¹

$T = 293$ K

Parallelepiped

$0.70 \times 0.25 \times 0.15$ mm

Green

Data collection

Siemens R3m/V diffractometer

θ – 2θ scans (4.19–29.30 $^\circ$

min⁻¹ in θ)

Absorption correction:

none

4031 measured reflections

1731 independent reflections

1454 observed reflections

$[F > 6.0\sigma(F)]$

$R_{\text{int}} = 0.004$

$\theta_{\text{max}} = 45^\circ$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 18$

2 standard reflections

monitored every 48

reflections

intensity variation: none

Refinement

Refinement on F

Final $R = 0.039$

$wR = 0.052$

$S = 1.21$

1454 reflections

159 parameters

H-atom parameters not refined

$w = [\sigma^2 F + 0.00157F^2]^{-1}$

$(\Delta/\sigma)_{\text{max}} = 0.00$

$\Delta\rho_{\text{max}} = 0.42$ e Å⁻³

$\Delta\rho_{\text{min}} = -1.03$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography* (1974, Vol. IV)

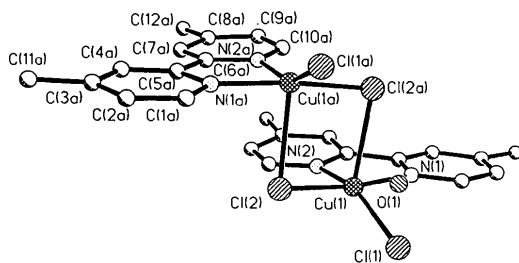


Fig. 1. Perspective view of the dimeric title compound.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	0.02516 (5)	0.59200 (3)	0.14877 (3)	0.0360 (2)
Cl(2)	0.19243 (12)	0.60491 (7)	0.25869 (6)	0.0465 (4)
Cl(1)	0.07384 (13)	0.71418 (6)	0.10239 (7)	0.0509 (4)
N(2)	0.03397 (33)	0.47099 (20)	0.14721 (17)	0.0324 (11)
N(1)	-0.13908 (36)	0.56968 (19)	0.06046 (19)	0.0325 (11)
C(6)	-0.07301 (42)	0.43639 (24)	0.09518 (22)	0.0320 (13)
C(12)	-0.00806 (54)	0.21732 (27)	0.13235 (30)	0.0579 (18)
C(10)	0.13014 (44)	0.42391 (26)	0.19230 (24)	0.0384 (15)
C(5)	-0.16854 (41)	0.49240 (22)	0.04350 (22)	0.0308 (13)
C(4)	-0.27683 (43)	0.46932 (23)	-0.01716 (23)	0.0361 (14)

C(7)	-0.09003 (44)	0.35437 (23)	0.09000 (23)	0.0365 (14)
C(9)	0.12241 (43)	0.34131 (25)	0.18838 (24)	0.0398 (15)
C(2)	-0.33513 (48)	0.60541 (24)	-0.04292 (24)	0.0402 (15)
C(3)	-0.36395 (44)	0.52598 (24)	-0.06278 (23)	0.0370 (14)
C(11)	-0.47909 (47)	0.50277 (28)	-0.13040 (27)	0.0498 (16)
C(8)	0.00983 (44)	0.30496 (26)	0.13722 (24)	0.0397 (15)
C(1)	-0.22470 (46)	0.62522 (26)	0.01712 (25)	0.0419 (15)
O(1)	0.0	0.82136 (29)	0.25000	0.0729 (20)

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Structure of Dimethyl(phenyl)phosphonium Tris(1,2-benzenedithiolato)tungsten(V)

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Abstract

The reaction of $[\text{WCl}_4(\text{PMe}_2\text{Ph})_3]$ with $\text{C}_6\text{H}_4(\text{SH})_2$ -1,2 in toluene gives dark brown $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$, which on standing in solution gives deep green $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$. The X-ray structure of $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ shows the tungsten to be coordinated by three $(\text{C}_6\text{H}_4\text{S}_2-1,2)^{2-}$ ligands with an average W—S distance of 2.386 (6) Å in a geometry which is halfway between octahedral and trigonal prismatic.

Comment

While dithiolate hydride complexes of molybdenum are well established, *e.g.* $[\text{MoH}_2(\text{C}_6\text{H}_4\text{S}_2-1,2)-(\text{PMe}_2\text{Ph})_2]$ (Lazarowych & Morris, 1987) and $[\text{MoH}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{3-}$ (Sellmann & Zapf, 1985), analogues of tungsten have proved elusive (Sellmann, Kern & Moll, 1991). As part of our investigation into the chemistry of molybdenum and tungsten hydrides with sulfur co-ligands (Burrow, Hills, Hughes, Lane, Morris & Richards, 1991), we have examined the reactions of $\text{C}_6\text{H}_4(\text{SH})_2$ -1,2 with the complex $[\text{WCl}_4(\text{PMe}_2\text{Ph})_3]$ in the hope of finding a route to new complexes of this type. The reaction



$[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ + unidentified products produced a dark oil which, from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, gave a dark brown complex formulated as $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ on the basis of ^1H and ^{31}P NMR spectral data [$\delta^{31}\text{P}$ -135.2 versus $\text{P}(\text{OMe})_3$]. A similar complex of molybdenum, *cis*- $[\text{Mo}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$, is known (Lazarowych & Morris, 1990). When a solution of $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ was allowed to stand, crystals of the

Table 2. Geometric parameters (Å, °)

Cu(1)—Cl(2)	2.255 (2)	C(3)—C(11)	1.497 (6)
Cu(1)—N(2)	2.035 (4)	Cu(1)—Cl(1)	2.274 (2)
Cu(1)—Cl(2a)	2.754 (2)	Cu(1)—N(1)	2.001 (3)
N(2)—C(6)	1.351 (5)	Cl(2)—Cu(1a)	2.754 (2)
N(1)—C(5)	1.349 (5)	N(2)—C(10)	1.338 (5)
C(6)—C(5)	1.483 (5)	N(1)—C(1)	1.364 (5)
C(5)—C(4)	1.380 (5)	C(6)—C(7)	1.388 (6)
C(3)—C(4)	1.402 (5)	C(12)—C(8)	1.482 (6)
C(7)—C(8)	1.398 (6)	C(10)—C(9)	1.391 (6)
C(9)—C(8)	1.388 (5)	C(2)—C(1)	1.370 (6)
C(2)—C(3)	1.393 (6)		
Cl(2)—Cu(1)—Cl(1)	93.9 (1)	N(2)—Cu(1)—N(1)	80.2 (1)
Cl(1)—Cu(1)—N(2)	152.5 (1)	Cl(1)—Cu(1)—Cl(2a)	109.5 (1)
Cl(1)—Cu(1)—N(1)	93.7 (1)	N(1)—Cu(1)—Cl(2a)	86.4 (1)
Cl(2)—Cu(1)—Cl(2a)	87.4 (1)	Cu(1)—N(2)—C(6)	114.4 (2)
N(2)—Cu(1)—Cl(2a)	96.9 (1)	C(6)—N(2)—C(10)	118.3 (3)
Cu(1)—Cl(2)—Cu(1a)	91.7 (1)	Cu(1)—N(1)—C(1)	126.0 (3)
Cu(1)—N(2)—C(10)	127.3 (3)	N(2)—C(6)—C(5)	115.1 (3)
Cu(1)—N(1)—C(5)	116.5 (2)	C(5)—C(6)—C(7)	122.8 (3)
C(5)—N(1)—C(1)	117.5 (3)	N(2)—C(10)—C(9)	122.5 (3)
N(2)—C(6)—C(7)	122.1 (3)	N(1)—C(5)—C(6)	113.6 (3)
N(1)—C(5)—C(4)	122.1 (3)	C(6)—C(5)—C(4)	124.3 (3)
C(6)—C(7)—C(8)	119.7 (3)	C(5)—C(4)—C(3)	120.9 (4)
C(4)—C(3)—C(2)	116.3(3)	C(10)—C(9)—C(8)	119.8 (4)
C(2)—C(3)—C(11)	121.7 (4)	C(3)—C(2)—C(1)	120.5 (4)
C(12)—C(8)—C(9)	122.5 (4)	C(4)—C(3)—C(11)	122.0 (4)
N(1)—C(1)—C(2)	122.7 (4)	C(12)—C(8)—C(7)	120.1 (4)
Cl(2)—Cu(1)—N(2)	94.8 (1)	C(7)—C(8)—C(9)	117.4 (4)
Cl(2)—Cu(1)—N(1)	171.5 (1)		

The complex was prepared by addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) to a solution containing 4,4'-dimethyl-2,2'-bipyridine (1 mmol) in freshly distilled ethanol. The resulting solution was refluxed and a green microcrystalline solid formed when the reaction mixture was cooled. The complex was recrystallized from acetonitrile.

SHELXTL/PC software (Sheldrick, 1991) was used to solve and refine the structure and collect data. Water H atoms were located from difference Fourier maps.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71122 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1026]

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