

Data reduction was carried out using *SHELX76* (Sheldrick, 1976). The coordinates of the non-H atoms were taken from Bonamico *et al.* (1965). All H atoms were included in the final cycle of refinement with $U(H) = 1.1U_{eq}(C)$ and $C-H = 0.98 \text{ \AA}$. Geometry calculations were carried out using *PARST* (Nardelli, 1983). Neither absorption nor extinction corrections were considered necessary.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond angles involving H atoms, least-squares-planes data and torsion angles, complete with H-atom torsion angles, have been deposited with the IUCr (Reference: MU1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Coordination Polymer Reminiscent of the Pleated Sheets Observed in Polypeptides: Diaqua-(2,2'-bipyridine-3,3'-dicarboxylato)-copper(II)

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Abstract

The preparation and crystal structure of [Cu(BPDC)-(H₂O)₂] (BPDC = C₁₂H₆N₂O₄²⁻, the dianion of 2,2'-bipyridine-3,3'-dicarboxylic acid) are described. The Cu atom is pentacoordinate; the BPDC ligands and water molecules form a distorted square-pyramidal geometry about the metal atom, BPDC residues linking Cu atoms to give a coordination polymer with head-to-tail alignment [*i.e.* *catena*-poly[diaquacopper(II)- μ -

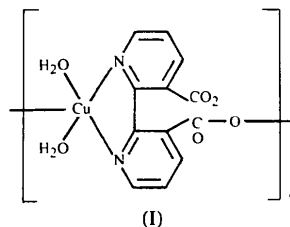
(2,2'-bipyridine-3,3'-dicarboxylato-*N,N'*:*O*)]}. Adjacent antiparallel chains are cross-linked by hydrogen bonds in a sheet-like structure reminiscent of the pleated sheets observed in polypeptides. The non-metallated O atoms of the carboxylate groups participate in hydrogen-bonding interactions with water molecules.

Comment

The use of metal complexes as probes of the structure of DNA has proved to be quite fruitful (Tullius & Dombroski, 1985; Sigman, 1986). Metal coordination complexes are also flexible reagents which permit observation of the effects of the central metal ion, the ligands and the coordination geometry on the binding event.

Square-pyramidal transition metal complexes usually adopt an octahedral configuration in solution by coordinating to a solvent molecule. In the solid state, the sixth coordination site can be filled by a ligand from an adjacent molecule, giving a coordination polymer (Chiang, Ho, Engen & Thompson, 1993). The head-to-tail nature of the coordination and organization in these materials is similar to that found in hydrogen-bonded systems. An advantage that coordination polymers may have over hydrogen-bonded systems is that the coordinate bond is typically much stronger than a hydrogen bond. The coordinate bond will also have a stronger directing influence on chain formation.

For these reasons, structural studies on metal complexes were undertaken in our laboratory (Ravikumar & Venkata Lakshmi, 1994). The title Cu^{II}-BPDC complex, (I) (where BPDC is 2,2'-bipyridine-3,3'-dicarboxylate), exists as an infinite coordination polymer in the solid state. A perspective view of the monomeric unit is shown in Fig. 1. Bond distances and angles (Table 2) are in good agreement with the values reported for related Cu^{II}-bipyridyl complexes (Stephens & Tucker, 1973; Newkome, Gupta & Fronczek, 1983; Goddard, Hemalatha & Rajasekharan, 1990).



The Cu atom adopts a five-coordinate geometry which may be described as distorted square pyramidal: it is bonded to two N atoms (N1 and N2) from one BPDC ligand, to two water molecules (O1W and O2W) and to a carboxylate O atom (O1ⁱ) from an adjacent BPDC residue [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$]. The base plane defined by the atoms N1, N2, O2W and O1ⁱ

exhibits considerable tetrahedral distortion: N1 and O2W lie 0.16 and 0.10 Å above the least-squares plane, while N2 and O1ⁱ lie 0.19 and 0.12 Å below it. The Cu atom is displaced 0.22 Å below this plane towards the axial ligand O1W. Similar distortions are observed in related five-coordinate transition metal complexes (Chiang, Ho, Engen & Thompson, 1993; Harrison & Hathaway, 1979; Tyagi, Hathaway, Kremer, Stratemir & Reinen, 1984). The Cu atom is bound to the carboxylate group in a *cis* conformation [Cu—O1ⁱ—C11ⁱ—O2ⁱ 3(1)°]. The two pyridine rings are not coplanar [C4—C5—C6—N1 149.6(6)°], presumably because of steric interaction between the two carboxylate groups. The dihedral angle between the planes of the two carboxylate groups is 166.1(8)°.

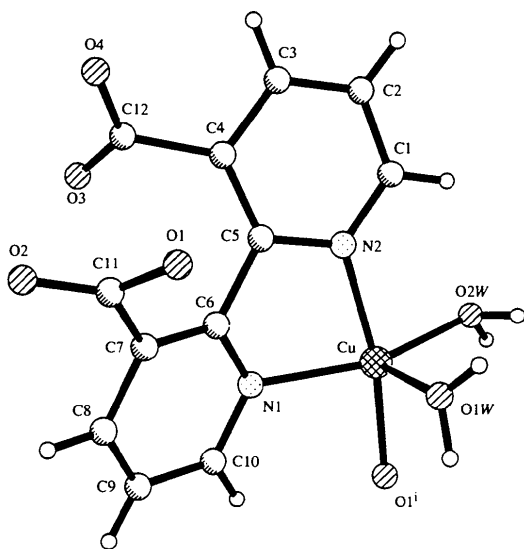


Fig. 1. A perspective view of the monomeric unit showing the atom-labelling scheme. Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$.

Secondary structure of the polymer. As alluded to above, the title compound exists as a coordination polymer. Infinite polymeric chains run along the *c* axis in the solid state (Fig. 2). These chains are linear and each BPDC ligand bridges two neighbouring Cu atoms in a head-to-tail fashion, *i.e.* —Cu(OOC—bpy)—Cu(OOC—bpy)—Cu(OOC—bpy)—. The Cu···Cu distances within the polymer chain are 6.91 Å. The polymer possesses a characteristic backbone structure with adjacent bipyridyl units oriented at an angle of 43.8° to one another. The dihedral angle between adjacent Cu—N1—N2—O2W—O1ⁱ equatorial planes is 47.6°.

It is interesting to note that adjacent chains are arranged in an antiparallel fashion. Interchain cross-linking is achieved through hydrogen bonding involving the non-metallated O atom of the carboxylate group and water molecules, with the formation of a sheet-

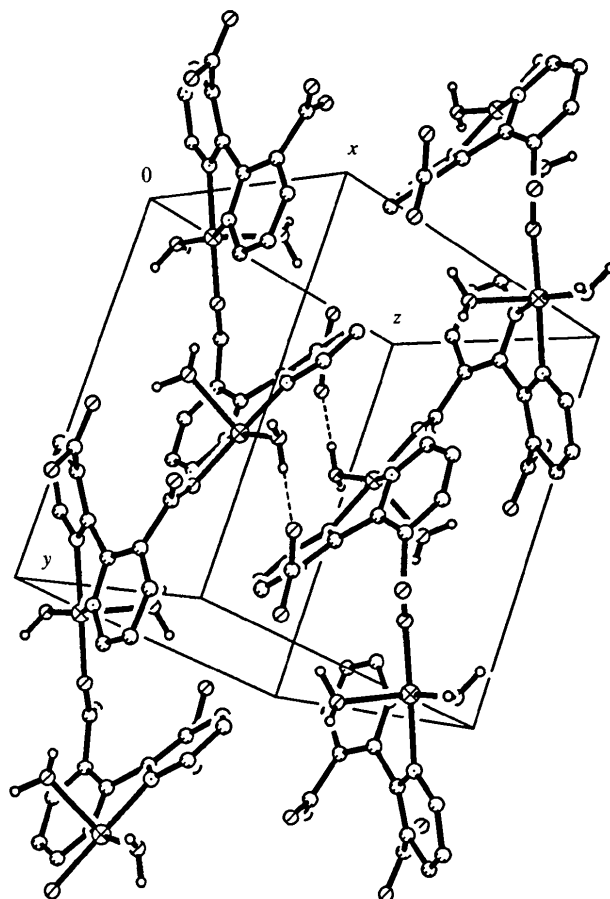


Fig. 2. A perspective view of the crystal packing showing both the head-to-tail arrangement of monomeric units along the polymer chain and the antiparallel relationship of adjacent chains. H atoms are omitted for clarity. Dashed lines indicate hydrogen bonds.

like structure somewhat reminiscent of the pleated sheets observed in polypeptides. Alternate chains in these sheets are related by an inversion centre, whereas polypeptide sheets are related by twofold symmetry axes. The shortest interchain Cu···Cu distance is 9.93 Å.

Hydrogen bonding. All uncoordinated carboxylate O atoms are linked to water molecules, forming a 'wire gauze'-like framework (Table 2). Interchain cross linking is achieved through hydrogen bonding between O2W and O3ⁱⁱⁱ [symmetry code: (iii) $-x, 2 - y, 2 - z$]. O4 is involved in hydrogen bonding to two water molecules.

Experimental

The ligand 2,2'-bipyridine-3,3'-dicarboxylic acid was prepared by the permanganate oxidation of 1,10-phenanthroline (Wimmer & Wimmer, 1983). Crystals of the complex were prepared in the following manner. To a mixture of 1 mmol of CuSO₄·5H₂O and 4.2 mmol of ligand, in an acetate-buffered 50:50 water—MeOH solvent system, was added 2 mmol of

NaBF₄. After addition of ascorbic acid (1.5 mmol) to effect reduction, evaporation of MeOH yielded pale blue crystals of the complex.

Crystal data

[Cu(C₁₂H₆N₂O₄)(H₂O)₂]

M_r = 341.7

Monoclinic

*P*2₁/*n*

a = 10.076 (1) Å

b = 11.372 (1) Å

c = 10.571 (1) Å

β = 100.33 (2)°

V = 1191.6 (2) Å³

Z = 4

D_x = 1.905 Mg m⁻³

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 12–21°

μ = 1.87 mm⁻¹

T = 293 K

Needle

0.18 × 0.16 × 0.15 mm

Pale blue

Data collection

Siemens R3m/V diffractometer

ω/2θ scans

Absorption correction:

empirical

T_{min} = 0.635, *T_{max}* = 0.718

1777 measured reflections

1567 independent reflections

1118 observed reflections

[*I* ≥ 3σ(*I*)]

R_{int} = 0.017

θ_{max} = 22.5°

h = 0 → 10

k = 0 → 12

l = -11 → 11

2 standard reflections

monitored every 98

reflections

intensity decay: <1%

Refinement

Refinement on *F*²

R = 0.048

wR = 0.045

S = 1.47

1118 reflections

190 parameters

w = 1/[σ²(*F*) + 0.0004*F*²]

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.24 e Å⁻³

Δρ_{min} = -0.28 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *SHELXTL-Plus*

(Sheldrick, 1990)

Table 2. Selected geometric parameters (Å, °)

Copper environment			
Cu—N1	2.065 (5)	Cu—N2	2.031 (5)
Cu—O1W	2.159 (4)	Cu—O2W	1.979 (4)
Cu—O1'	1.949 (4)		
O1W—Cu—O2W	100.5 (2)	N2—Cu—O2W	91.8 (2)
N2—Cu—O1W	90.1 (2)	N1—Cu—O2W	158.2 (2)
N1—Cu—O1W	99.4 (2)	N1—Cu—N2	79.5 (2)
O2W—Cu—O1'	97.5 (2)	O1W—Cu—O1'	93.6 (2)
N2—Cu—O1'	169.2 (2)	N1—Cu—O1'	89.9 (2)
2,2'-Bipyridine-3,3'-dicarboxylate ligand			
O1—C11	1.280 (8)	O2—C11	1.231 (9)
O3—C12	1.228 (8)	O4—C12	1.270 (7)
N1—C6	1.360 (8)	N1—C10	1.340 (7)
N2—C1	1.345 (8)	N2—C5	1.361 (9)
C1—C2	1.380 (8)	C2—C3	1.356 (9)
C3—C4	1.413 (9)	C4—C5	1.396 (9)
C4—C12	1.538 (9)	C5—C6	1.488 (9)
C6—C7	1.392 (9)	C7—C8	1.400 (9)
C7—C11	1.522 (9)	C8—C9	1.377 (8)
C9—C10	1.376 (9)		
C6—N1—C10	120.6 (5)	C1—N2—C5	120.6 (5)
N2—C1—C2	121.7 (6)	C1—C2—C3	118.5 (6)
C2—C3—C4	121.2 (6)	C3—C4—C12	116.5 (5)
C3—C4—C5	117.6 (6)	C5—C4—C12	125.2 (5)
N2—C5—C4	119.9 (6)	C4—C5—C6	126.3 (6)
N2—C5—C6	113.6 (5)	N1—C6—C5	112.9 (5)
C5—C6—C7	126.0 (5)	N1—C6—C7	121.1 (5)
C6—C7—C11	126.1 (6)	C6—C7—C8	116.4 (6)
C8—C7—C11	117.1 (6)	C7—C8—C9	121.4 (6)
C8—C9—C10	118.7 (5)	N1—C10—C9	120.8 (5)
O2—C11—C7	118.3 (6)	O1—C11—C7	113.7 (6)
O1—C11—O2	127.9 (5)	O4—C12—C4	115.9 (5)
O3—C12—C4	117.9 (5)	O3—C12—O4	126.0 (6)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H2W1...O4 ⁱ	0.92	1.81	2.728 (5)	172
O1W—H1W1...O2 ⁱⁱ	0.82	2.01	2.760 (6)	152
O2W—H1W2...O4 ⁱⁱ	0.79	1.98	2.706 (6)	154
O2W—H2W2...O3 ⁱⁱⁱ	0.93	1.77	2.699 (6)	174

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $-x, 2 - y, 2 - z$.

H atoms were clearly visible in difference maps at an intermediate stage of the refinement; they were positioned geometrically and included in the structure-factor calculations as riding atoms with fixed isotropic displacement parameters. *SHELXTL-Plus* (Sheldrick, 1990) was used for data processing, structure solution and refinement, and *PARST* (Nardelli, 1983) for the final interpretation of molecular geometry and crystal packing. All calculations were performed on a VAX 3100 workstation.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cu	0.0520 (1)	1.0170 (1)	1.2137 (1)	0.0212 (3)
O1	0.4026 (4)	0.6754 (3)	1.2222 (4)	0.022 (2)
O2	0.5402 (4)	0.7107 (3)	1.0802 (5)	0.035 (2)
O3	0.2759 (4)	0.7694 (4)	0.8509 (4)	0.025 (2)
O4	0.2650 (4)	0.5816 (3)	0.9074 (4)	0.027 (2)
N1	0.2300 (5)	1.0095 (4)	1.1431 (5)	0.016 (2)
N2	0.0345 (5)	0.8558 (4)	1.1296 (5)	0.018 (2)
C1	-0.0800 (7)	0.7925 (5)	1.1086 (7)	0.022 (3)
C2	-0.0910 (7)	0.6896 (5)	1.0382 (6)	0.026 (3)
C3	0.0150 (7)	0.6555 (5)	0.9840 (7)	0.021 (3)
C4	0.1358 (7)	0.7215 (5)	1.0017 (6)	0.014 (2)
C5	0.1451 (6)	0.8189 (5)	1.0833 (6)	0.013 (3)
C6	0.2643 (7)	0.8972 (5)	1.1187 (6)	0.013 (3)
C7	0.3988 (7)	0.8637 (5)	1.1302 (7)	0.013 (3)
C8	0.4941 (6)	0.9545 (5)	1.1463 (6)	0.019 (3)
C9	0.4568 (7)	1.0698 (5)	1.1591 (7)	0.022 (3)
C10	0.3237 (6)	1.0945 (5)	1.1621 (6)	0.019 (3)
C11	0.4524 (7)	0.7383 (5)	1.1419 (7)	0.018 (3)
C12	0.2372 (6)	0.6900 (5)	0.9143 (6)	0.015 (3)
O1W	0.1184 (4)	0.9361 (4)	1.3990 (3)	0.029 (2)
O2W	-0.1447 (4)	1.0259 (3)	1.2107 (4)	0.020 (2)

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The *trans* Influence of the Silyl Ligand. Structure of *trans*-[PtCl(SiPh₃)(PMe₂Ph)₂]

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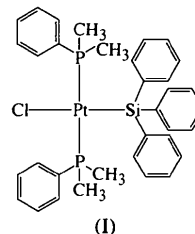
Abstract

In the crystal structure of *trans*-chlorobis(dimethylphenylphosphine)(triphenylsilyl)platinum(II), [PtCl(C₁₈H₁₅Si)(C₈H₁₁P)₂], the Pt atom coordinates to one Si and one Cl atom, and to two P atoms in mutual *trans* positions. The coordination geometry is distorted square planar with distances Pt—Si 2.321 (2), Pt—Cl 2.465 (2) and Pt—P 2.282 (2) and 2.322 (2) Å. The silyl ligand shows a very large *trans* influence on the Pt—Cl distance.

Comment

From IR spectroscopy studies, Chatt, Eaborn & Ibekwe (1966) have postulated that silicon should have an exceptionally high ground-state *trans* influence. This was further supported by a crystal structure determination of *trans*-[PtCl(SiMePh₂)(PMe₂Ph)₂], which revealed a Pt—Cl distance of 2.45 (1) Å (Kapoor, 1968), almost 0.15 Å longer than in PtCl₄²⁻ (Bengtsson & Os-

karsson, 1992). The crystal structure determination of this silicon compound was based on film data, resulting in fairly high e.s.d.'s of distances and angles. For a quantitative discussion of the *trans* influence more accurate data are needed. For this purpose we decided to determine the structure of *trans*-[PtCl(SiPh₃)(PMe₂Ph)₂], (I).



The compound is composed of tetrahedrally distorted square-planar mononuclear [PtCl(SiPh₃)(PMe₂Ph)₂] complexes. The shortest Pt···Pt distance is 8.954 (2) Å. The structure and atomic numbering are shown in Fig. 1. In spite of the fact that the crystal structure is determined far below the melting point, 443 K (Chatt, Eaborn, Ibekwe & Kapoor, 1970), the displacement ellipsoids of the C atoms, especially in the phenyl rings C(10)–C(15) and C(50)–C(55), show large anisotropic movements of these atoms. The angles about the Pt atom vary from 85.73 (6) to 95.05 (7)°. This distortion is most likely caused by the large and bulky ligands. Deviations from the least-squares plane through the coordination plane are Pt 0.0025 (3), Si –0.179 (2), Cl –0.370 (2), P(1) 0.201 (2) and P(2) 0.184 (2) Å. The methyl group C(26) (Fig. 1) is approximately located in the coordination plane (0.214 Å out of the least-squares plane). This causes some repulsion between the phosphine and the silyl ligand, the shortest contact being C(26)···C(40) 3.22 (1) Å. The interaction moves the whole phosphine ligand towards the chloride ion, making the Cl—Pt—P(2) angle as small as 85.73 (6)°. The dihedral angle between the least-squares planes through the phenyl rings C(10)–C(15) and C(50)–C(55) is rather small, at 16° (Fig. 1). The closest non-H contact between these phenyl rings is between C(10) and C(50), the distance being 3.25 Å and indicating van der Waals contacts. The phosphine ligands push the chloride ion out of the coordination plane since the P(1)···Cl [3.286 (3) Å], C(16)···Cl [3.29 (1) Å] and P(2)···Cl [3.258 (3) Å] distances are all shorter than the van der Waals distances. It may be concluded that the distortion of the coordination geometry is most likely caused by intramolecular contacts.

The Pt—P distances [2.282 (2) and 2.322 (2) Å] do not differ significantly from those distances found in other *trans*-phosphines, e.g. *trans*-[PtCl₂(PEt₃)₂] (2.300 Å; Messmer & Amma, 1966) and those compounds in Table 3. The difference between Pt—P(1) [2.282 (2) Å] and Pt—P(2) [2.323 (2) Å] is highly sig-

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