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 Cu₂Cl₂ 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" 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-\(\mu\)-chloro(2,2’-bipyridine)copper(II)] reported previously (Garland, Grandjean, Spodine, Atria & Manzur, 1988).

The reported dimeric complex has a Cu\(_2\)Cl\(_2\) 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 non-parallel Cl(1)–Cu(1)–Cl(1) 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-\(\mu\)-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\(_2\)Cl\(_2\) units are quite different. In the catena compound the Cu\(_2\)Cl\(_2\) 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**

\[
\begin{align*}
[CuCl_2(C_6H_12N_2)_2].0.5H_2O & : & D_e = 1.657 \text{ Mg m}^{-3} \\
M_r = 327.7 & : & \text{Mo } K\alpha \text{ radiation} \\
\text{Monoclinic} & : & \lambda = 0.71073 \text{ Å} \\
C2/c & : & \text{Cell parameters from 25 reflections} \\
a = 9.134 (4) \text{ Å} & : & \theta = 5-20^\circ \\
b = 16.801 (6) \text{ Å} & : & \mu = 2.052 \text{ mm}^{-1} \\
c = 17.335 (8) \text{ Å} & : & T = 293 \text{ K} \\
\beta = 99.15 (3)^\circ & : & \text{Parallelepiped} \\
\nu = 2626 (2) \text{ Å}^3 & : & 0.70 \times 0.25 \times 0.15 \text{ mm} \\
Z = 8 & : & \text{Green}
\end{align*}
\]

**Data collection**

Siemens R3m/V diffractometer

\[
\begin{align*}
R_{int} & = 0.004 \\
\theta_{max} & = 45^\circ \\
\theta-2\theta & \text{ scans (4.19-29.30° min}^{-1} \text{ in } \theta \\
k & = 0 \rightarrow 18 \\
\text{Absorption correction:} & \text{none} \\
4031 & \text{measured reflections} \\
1731 & \text{independent reflections} \\
1454 & \text{observed reflections} \\
[F>6.0\sigma(F)] & \text{monitored every 48 reflections} \\
\text{intensity variation: none}
\end{align*}
\]

**Refinement**

Refinement on \(F\)

\[
\begin{align*}
\text{Final } R & = 0.039 \\
\text{wR} & = 0.052 \\
S & = 1.21 \\
1454 & \text{reflections} \\
159 & \text{parameters} \\
\text{H-atom parameters not refined}
\end{align*}
\]

\[
\begin{align*}
\omega = [\sigma^2 F + 0.00157 F^2]^{-1} \\
(\Delta/\sigma)_{max} & = 0.00 \\
\Delta \rho_{max} & = 0.42 \text{ e Å}^{-3} \\
\Delta \rho_{min} & = -1.03 \text{ e Å}^{-3} \\
\text{Atomic scattering factors from International Tables} \\
\text{for X-ray Crystallography (1974, Vol. IV)}
\end{align*}
\]

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

\[
\begin{align*}
U_{eq} \text{ is defined as one third of the trace of the orthogonalized } U_{ij} \text{ tensor.}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{cccccc}
\text{Cu(1)} & x & y & z & U_{eq} \\
0.02516 (5) & 0.59200 (3) & 0.14877 (3) & 0.0360 (2) \\
(2) & 0.19243 (12) & 0.60491 (7) & 0.25869 (6) & 0.0465 (4) \\
(11) & 0.07384 (13) & 0.71418 (6) & 0.10239 (7) & 0.0509 (4) \\
(12) & 0.03397 (33) & 0.47099 (20) & 0.14721 (17) & 0.0324 (11) \\
(13) & -0.13908 (36) & 0.56968 (19) & 0.06046 (19) & 0.0325 (11) \\
(14) & -0.07031 (42) & 0.43639 (24) & 0.09518 (22) & 0.0320 (13) \\
(15) & -0.00806 (54) & 0.21732 (27) & 0.13235 (30) & 0.0579 (18) \\
(16) & 0.13014 (44) & 0.42391 (26) & 0.19230 (24) & 0.0384 (15) \\
(17) & -0.16854 (41) & 0.49240 (22) & 0.04350 (22) & 0.0308 (13) \\
(18) & -0.27683 (43) & 0.46932 (23) & -0.01716 (23) & 0.0361 (14)
\end{array}
\end{align*}
\]
Table 2. Geometric parameters (Å, °)

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The complex was prepared by addition of CuCl₂·2H₂O (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 acetone/nitrite.

SHELXL/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]

References


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