

|               |            |              |          |
|---------------|------------|--------------|----------|
| Te2—C12       | 2.388 (5)  | N3—C3        | 1.13 (2) |
| Te2—C110      | 2.628 (5)  | C3—C33       | 1.41 (2) |
| Te2—C114      | 2.454 (5)  | N4—C4        | 1.20 (3) |
| Te2—C115      | 2.315 (5)  | C4—C44       | 1.35 (3) |
| Te3—C14       | 2.663 (5)  | N5—C5        | 1.14 (2) |
| Te3—C15       | 2.329 (5)  | C5—C55       | 1.46 (2) |
| Te3—C16       | 2.403 (5)  | N6—C6        | 1.09 (3) |
| Te3—C19       | 2.482 (5)  | C6—C66       | 1.43 (4) |
| Te3—C111      | 2.464 (5)  | N7—C7        | 1.14 (3) |
| Al1—N1        | 1.967 (14) | C7—C77       | 1.38 (3) |
| Al1—N2        | 1.952 (12) | N8—C8        | 1.12 (3) |
| Al1—N3        | 1.922 (12) | C8—C88       | 1.40 (3) |
| Al2—N4        | 1.99 (2)   | N9—C9        | 1.15 (2) |
| Al2—N5        | 1.947 (13) | C9—C99       | 1.37 (2) |
| Al2—N6        | 1.97 (2)   |              |          |
| C13—Te1—C18   | 89.3 (2)   | C15—Te3—C111 | 87.6 (2) |
| C17—Te1—C113  | 89.0 (2)   | C15—Te3—C14  | 87.5 (2) |
| C112—Te1—C13  | 88.6 (2)   | C16—Te3—C19  | 89.3 (2) |
| C112—Te1—C17  | 91.3 (2)   | C16—Te3—C111 | 89.1 (2) |
| C112—Te1—C18  | 88.1 (2)   | C19—Te3—C14  | 91.6 (2) |
| C112—Te1—C113 | 86.9 (2)   | N2—Al1—N1    | 89.9 (5) |
| C113—Te1—C18  | 92.9 (2)   | N3—Al1—N1    | 90.9 (5) |
| C11—Te2—C110  | 90.3 (2)   | N3—Al1—N2    | 91.2 (5) |
| C12—Te2—C11   | 90.6 (2)   | N5—Al2—N4    | 89.8 (5) |
| C12—Te2—C114  | 89.4 (2)   | N5—Al2—N6    | 90.2 (5) |
| C115—Te2—C11  | 88.9 (2)   | N5—Al2—N7    | 88.7 (5) |
| C115—Te2—C12  | 89.4 (2)   | N5—Al2—N8    | 91.3 (5) |
| C115—Te2—C110 | 88.2 (2)   | N7—Al2—N6    | 91.4 (9) |
| C115—Te2—C114 | 89.3 (2)   | N8—Al2—N4    | 91.1 (8) |
| C15—Te3—C16   | 90.1 (2)   | N8—Al2—N6    | 88.4 (9) |
| C15—Te3—C19   | 87.5 (2)   |              |          |

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## A Copper(II) Complex of a New Chiral Tridentate Imidazoline Ligand

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### Abstract

The title compound, {2,6-bis[(4*R*,5*R*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl-*N*<sup>1</sup>]pyridine-*N*}chloro-copper(II) hexafluorophosphate 0.5-methanol solvate, [CuCl(C<sub>39</sub>H<sub>41</sub>N<sub>5</sub>)]PF<sub>6</sub>·0.5CH<sub>3</sub>OH, is the first example of a metal complex containing the new chiral ligand, 2,6-bis[(4*R*,5*R*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl]pyridine. Complexation of the ligand to the Cu atom results in only a slight distortion from idealized C<sub>2</sub> symmetry in the crystal in spite of its less symmetrical environment.

### Comment

The compound 2,6-bis[(4*R*,5*R*)-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl]pyridine has been prepared in an enantiomerically pure form as part of a study to evaluate its properties as a chiral ligand for asymmetric catalysis (Pfaltz, 1996). The structure of a copper complex, (I), has been determined in order to establish the geometry of the ligand when it is coordinated to the metal.

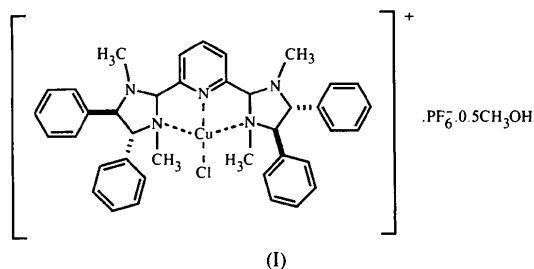
The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). Full-matrix least-squares refinements made by the *SHELXL93* program (Sheldrick, 1993) were carried out using anisotropic displacement parameters for Te, Al, Cl atoms and for C and N atoms of the free solvent molecule. H atoms were included in idealized positions with displacement parameters fixed to 1.2 times those of the C atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: own program. Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1301). Services for accessing these data are described at the back of the journal.

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Complex (I) crystallizes in the chiral space group  $P2_12_12_1$  with one molecule of the copper complex and half a molecule of methanol in the asymmetric unit (Fig. 1). The coordination sphere of the  $\text{Cu}^{\text{II}}$  atom is distorted square planar. The N atoms of the tridentate ligand and the Cu atom are coplanar (r.m.s. deviation 0.09 Å), but the Cl atom is bent  $10^\circ$  out of the plane, away from the methanol of crystallization. The coordinating Cu—N distances are typical for distances of correspondingly hybridized N atoms coordinated to a Cu atom (Allen & Kennard, 1993).

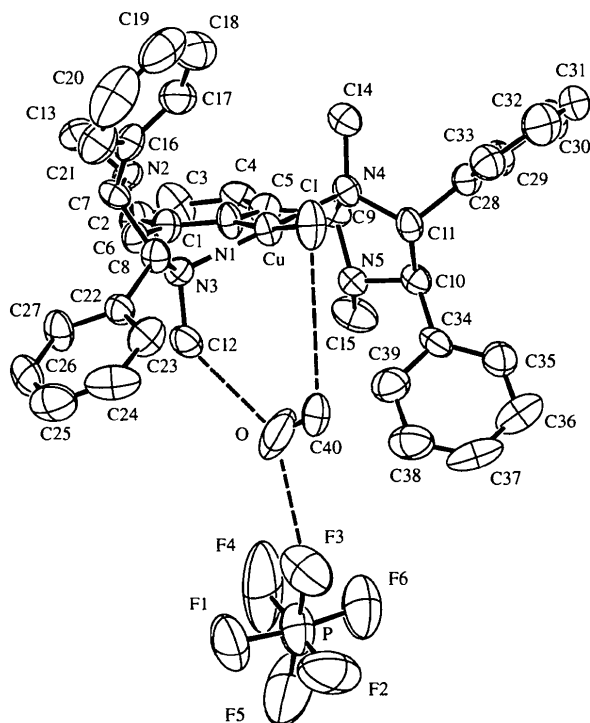


Fig. 1. The molecular structure of (I), showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

Apart from the Cl atom, the expected  $C_2$  symmetry of the cation is largely retained in the crystal in spite of a less symmetrical environment ( $C_1$ ). Torsion angles are a sensitive indicator of conformation and those torsion angles in the ligand that would be equivalent under  $C_2$  symmetry agree within  $4^\circ$ . Thus, the torsion angle

$\text{N1—C1—C6—N3}$  [ $-28(1)^\circ$ ] compares favorably with  $\text{N1—C5—C9—N4}$  [ $-33(1)^\circ$ ], while  $\text{N1—C1—C6—N2}$  [ $82(1)^\circ$ ] is close to  $\text{N1—C5—C9—N5}$  [ $78(1)^\circ$ ]. The  $C_2$  symmetry even extends to the phenyl groups attached to the imidazolidine rings such that  $\text{N5—C10—C34—C39}$  [ $-31(1)^\circ$ ] is almost identical to  $\text{N2—C7—C16—C17}$  [ $-31(1)^\circ$ ], and  $\text{N4—C11—C28—C29}$  [ $-79(1)^\circ$ ] only differs by  $8^\circ$  from  $\text{N3—C8—C22—C27}$  [ $-71(1)^\circ$ ]. The angles between the mean plane through the central pyridine ring ( $p_1$ ) and planes of the four phenyl groups ( $p_2$ – $p_5$ ) follow the same trend. The angle between  $p_1$  and  $p_2$  (C16–C21) at  $51.6(3)^\circ$  is almost the same as that between  $p_1$  and  $p_3$  (C34–C39) [ $51.4(2)^\circ$ ], and that between  $p_1$  and  $p_4$  (C22–C27) [ $31.2(3)^\circ$ ] is not significantly different from that between  $p_1$  and  $p_5$  (C28–C33) [ $31.1(3)^\circ$ ].

It is instructive to compare the coordination geometry of (I) with analogous complexes of 2,6-bis-(pyrrolidin-2-yl)pyridine and 2,6-bis(4-isopropyl-1,3-oxazolin-2-yl)pyridine. All three tridentate ligands contain five-membered heterocyclic rings attached to the *ortho* positions of a pyridine ring. In both [2,6-bis(4-isopropyl-1,3-oxazolin-2-yl)pyridine- $N,N,N'$ ]trichlororhodium monohydrate ([ $(S,S)$ -ip-pybox]RhCl<sub>3</sub>) (Nishiyama, Kondo, Nakamura & Itoh, 1991) and aqua[2,6-bis(pyrrrolidin-2-yl)pyridine]copper(II) diperchlorate dihydrate (Bernauer, Gretillat, Stoeckli-Evans & Warmuth, 1993), the mean plane of the pyridine ring is almost coplanar with the mean plane through the metal atom and the three N atoms of the tridentate ligand, although in the latter compound, the pyrrolidine rings are themselves not planar. In (I), however, the Cu—N1 bond is twisted and the angle between the pyridine ring and the mean plane through Cu, N1, N3 and N4 is  $14.1(3)^\circ$ . This has a direct influence on the positions of the substituents attached to N3 and N4, for the bonds from these two N atoms to their attendant methyl groups, C12 and C14, are almost perpendicular to the coordination plane of the metal [torsion angles  $\text{N1—Cu—N3—C12}$   $88(1)$  and  $\text{N1—Cu—N4—C14}$   $91(1)^\circ$ ].

Major inter-moiety interactions involve the methanol of crystallization, which probably forms a hydrogen bond to one F atom of the  $\text{PF}_6^-$  anion. Although the H atom attached to the O atom could not be located in the difference Fourier map, the  $\text{O} \cdots \text{F3}$  distance of  $2.97(2)$  Å is well within the range of observed distances for hydrogen bonds between these atoms (Jeffrey & Saenger, 1991). The  $\text{O} \cdots \text{C12}$  and  $\text{C40} \cdots \text{Cl}$  distances are longer [ $3.48(2)$  and  $4.08(3)$  Å, respectively], but being amongst the shortest inter-moiety distances, they suggest that the methanol molecule takes up a bridging position between the anion and the cation (Fig. 1). It should, however, be noted that distances involving C40 and O should be treated with caution because of the large atomic displacement parameters associated with these atoms. Indeed, the  $\text{C40—O}$  distance is over-short [ $1.23(3)$  Å], possibly indicating unresolved disorder.

## Experimental

For the preparation of (I), tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.13 mmol) and 2,6-bis(1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)pyridine (0.15 mmol) were dissolved in dry methylene chloride. The resulting orange solution turned green on exposure to air. Removal of solvent and recrystallization from neat methanol after an unsuccessful attempt using chloroform/methanol resulted in a 20% yield of deep-blue crystals.

### Crystal data

|  |  |
|--|--|
| [CuCl(C <sub>39</sub> H <sub>41</sub> N <sub>5</sub> )]PF <sub>6</sub> ·0.5CH <sub>4</sub> O | Mo K $\alpha$ radiation<br>$\lambda = 0.71069 \text{ \AA}$ |
| $M_r = 839.75$   | Cell parameters from 25 reflections                        |
| Orthorhombic   | $\theta = 9.00\text{--}20.25^\circ$                        |
| $P2_12_12_1$   | $\mu = 0.720 \text{ mm}^{-1}$                              |
| $a = 14.636 (2) \text{ \AA}$   | $T = 293 \text{ K}$  |
| $b = 15.185 (3) \text{ \AA}$   | Rectangular prism  |
| $c = 17.928 (2) \text{ \AA}$   | $0.35 \times 0.21 \times 0.18 \text{ mm}$                  |
| $V = 3984.4 (10) \text{ \AA}^3$  | Deep blue  |
| $Z = 4$  |  |
| $D_x = 1.40 \text{ Mg m}^{-3}$   |  |
| $D_m$ not measured   |  |

### Data collection

|  |                         |
|--|-------------------------|
| Enraf-Nonius CAD-4 diffractometer      | $h = -18 \rightarrow 0$ |
| $\omega$ - $2\theta$ scans             | $k = -18 \rightarrow 0$ |
| Absorption correction: none            | $l = 0 \rightarrow 22$  |
| 4490 measured reflections              | 3 standard reflections  |
| 4490 independent reflections           | frequency: 30 min       |
| 2291 reflections with $I > 2\sigma(I)$ | intensity decay: none   |
| $\theta_{\max} = 26.31^\circ$          |                         |

### Refinement

|   |  |
|---|--|
| Refinement on $F^2$                               | $(\Delta/\sigma)_{\max} < 0.001$   |
| $R(F) = 0.059$                                    | $\Delta\rho_{\max} = 0.475 \text{ e \AA}^{-3}$                                   |
| $wR(F^2) = 0.179$                                 | $\Delta\rho_{\min} = -0.622 \text{ e \AA}^{-3}$                                  |
| $S = 1.007$                                       | Extinction correction: none  |
| 4490 reflections                                  | Scattering factors from <i>International Tables for Crystallography</i> (Vol. C) |
| 500 parameters                                    | Absolute configuration: Flack (1983)   |
| H atoms: see below                                | Flack parameter = 0.01 (4)   |
| $w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 1.9156P]$ |  |
| where $P = (F_o^2 + 2F_c^2)/3$                    |  |

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|          |           |          |           |
|----------|-----------|----------|-----------|
| Cu—N1    | 1.927 (6) | Cu—N4    | 2.116 (7) |
| Cu—N3    | 2.114 (7) | Cu—Cl    | 2.173 (2) |
| N1—Cu—N3 | 80.9 (3)  | N1—Cu—Cl | 172.7 (3) |
| N1—Cu—N4 | 81.2 (3)  | N3—Cu—Cl | 101.7 (2) |
| N3—Cu—N4 | 161.6 (3) | N4—Cu—Cl | 96.6 (2)  |

All non-H atoms were refined anisotropically. The methanol solvent molecule was included in the refinement with half occupancy (based on chemical analysis). The H atoms were refined using a riding model, including torsional freedom for methyl and OH groups, with  $U(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ ,  $1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for others.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1995). Cell refinement: CAD-4 EXPRESS. Data reduction: DATAP

(Coppens, Leiserowitz & Rabinovich, 1965). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEPII (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1153). Services for accessing these data are described at the back of the journal.

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## [6,6'-Bis(benzimidazol-2-yl-*N*<sup>3</sup>)-2,2'-bipyridine]dichlorocobalt(II)-Dimethylformamide (1/2)

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## Abstract

The title complex, [CoCl<sub>2</sub>(C<sub>24</sub>H<sub>16</sub>N<sub>6</sub>)]·2C<sub>3</sub>H<sub>7</sub>NO, has been prepared from cobalt chloride and 6,6'-dibenzimidazolyl-2,2'-bipyridine (DBBP). The metal center is coordinated in a distorted tetrahedral configuration to two Cl<sup>-</sup> ions and to two N donor atoms of the DBBP ligand which acts bidentately. The Co—N distances are 2.033 (4)  $\text{\AA}$  and the Co—Cl distances are 2.2300 (18)  $\text{\AA}$ . The coordination angles lie between 102.61 (13) and 118.13 (18) $^\circ$ . The complex has C<sub>2</sub> symmetry.