

This work was partially supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo a Pesquisa do Estado de Minas Gerais (FAPEMIG).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1062–1064

[2,6-Bis(2-pyrimidinylthiomethyl)pyridine]-dichlorocopper(II) Methanol Solvate

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(Received 17 June 1993; accepted 2 December 1993)

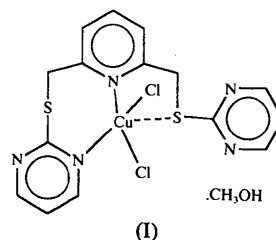
Abstract

In the title compound, [CuCl₂(C₁₅H₁₃N₅S₂)]·CH₃OH, the Cu²⁺ ion has square-pyramidal coordination geometry. The basal plane of the pyramid is formed

by two Cl⁻ ions, one pyridine N atom and one pyrimidine N atom. The fifth coordination site is occupied by the S atom of a thiomethyl group. The methanol molecule occupies an otherwise empty space in the structure.

Comment

The coordination chemistry of 2,6-bis(*R*-thiomethyl)-pyridine changes considerably with the nature of the *R* group (Teixidor, Sánchez-Castelló, Lucena, Escriche, Kivekäs, Sundberg & Casabó, 1991). The present ligand, 2,6-bis(2-pyrimidinylthiomethyl)pyridine, in the title compound, (I), has seven potential donor atoms, which afford a large number of different possible coordination modes. The title complex is a new example of this series and shows an asymmetric coordination mode of the multidentate ligand.



The structure consists of molecular complex units and methanol molecules. The complex is depicted in Fig. 1. The ligand is coordinated in a tridentate manner to the Cu²⁺ ion. The two Cl⁻ ions and two ligand N atoms form the equatorial plane around the Cu²⁺ ion. The fifth coordination site is occupied by the S atom of a thiomethyl group. The Cu—Cl distances are similar whereas Cu—N(1) and

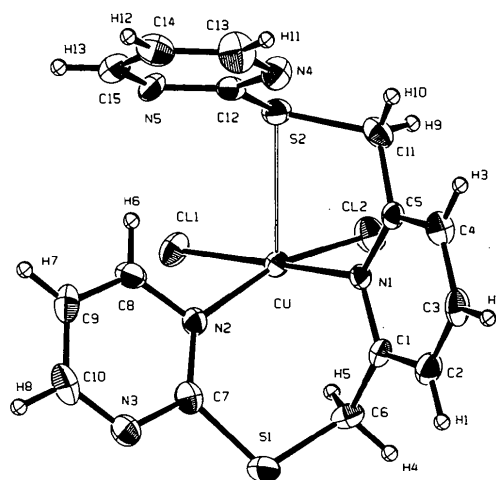


Fig. 1. ORTEP (Johnson, 1975) plot of the title compound. Displacement ellipsoids are shown at 30% probability levels, except for those of the H atoms which are drawn with an isotropic displacement factor of 1.0.

Cu—N(2) differ (Table 2). The axial Cu—S(2) distance is elongated. No other angles around the Cu atom other than Cl(1)—Cu—N(1) and Cl(2)—Cu—N(2) deviate much from the expected values for square-pyramidal geometry. Distortions are a result of the bulky ligand which forces the Cu^{II} to adopt the observed geometry. The methanol molecule is disordered so that the O and C atoms could not be reliably distinguished. However, the structure was refined with C and O atoms of the solvent molecules in the positions as indicated in Table 1. Only H(C) atoms of methanol were included in final calculations.

Experimental

The title compound was synthesized when CuCl₂·2H₂O (0.052 g, 0.30 mmol), dissolved in methanol (2 cm³), was added to a solution of 2,6-bis(2-pyrimidinylthiomethyl)pyridine (0.1 g, 0.30 mmol) in methanol (2 cm³). A green crystalline solid suitable for X-ray diffraction analysis was obtained which was filtered off, washed with ethyl acetate (10 cm³) and vacuum dried. Yield: 60% (0.089 g). Analysis: calculated for C₁₆H₁₇Cl₂CuN₅O₂S₂, C 38.9, H 3.5, N 14.18, S 13.0, Cl 14.4%; found, C 38.6, H 3.1, N 14.3, S 13.2, Cl 14.8%.

In the preparation of 2,6-bis(2-pyrimidinylthiomethyl)pyridine, KOH 85% (2.09 g, 31.7 mmol) in ethanol (200 cm³) was stirred under reflux for 30 min with 2-mercaptopyrimidine (3.55 g, 31.7 mmol). Then, this solution was added to a solution of 2,6-bis(bromomethyl)pyridine (4.2 g, 15.8 mmol) in ethanol (100 cm³) and was stirred under reflux for 1 h. The KBr formed was filtered out and discarded. The filtrate was evaporated under reduced pressure and the resulting yellow solid was recrystallized in water to afford a white solid. Yield: 53% (2.74 g). Analysis: calculated for C₁₅H₁₃N₅S₂, C 55.0, H 4.0, N 21.4, S 19.8%; found, C 55.1, H 4.1, N 20.8, S 19.3%. ¹H NMR (CDCl₃): δ 4.49 (s, 4, py—CH₂—S); δ 7.62 (m, 11, aromatic).

Dehydrated and deoxygenated solvents were used in the syntheses. 2,6-Bis(bromomethyl)pyridine was prepared according to the procedure reported by Offermann & Vögtle (1977). 2-Mercaptopyrimidine is commercially available (Aldrich) and was used as received. Microanalyses were performed on a Perkin-Elmer 240-B instrument. Proton NMR spectra were recorded on a Bruker 400 MHz AC instrument.

Crystal data

[CuCl ₂ (C ₁₅ H ₁₃ N ₅ S ₂)]· CH ₃ OH	$D_x = 1.640 \text{ Mg m}^{-3}$
$M_r = 493.92$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71069 \text{ \AA}$
$P2_1/n$	Cell parameters from 17 reflections
$a = 8.561 (3) \text{ \AA}$	$\theta = 4.5 - 13^\circ$
$b = 14.107 (4) \text{ \AA}$	$\mu = 1.58 \text{ mm}^{-1}$
$c = 16.582 (5) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 92.72 (3)^\circ$	Prismatic
$V = 2000 (1) \text{ \AA}^3$	$0.25 \times 0.15 \times 0.05 \text{ mm}$
$Z = 4$	Green

Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.062$
	$\theta_{\text{max}} = 25^\circ$

ω -2 θ scans

Absorption correction:
none

3945 measured reflections
3686 independent reflections
1716 observed reflections
[$I > 2\sigma(I)$]

Refinement

Refinement on F

$R = 0.064$

$wR = 0.056$

$S = 1.31$

1716 reflections

244 parameters

H-atom parameters not refined

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 17$

$l = -20 \rightarrow 20$

3 standard reflections
monitored every 150
reflections

intensity variation: -2.1%

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.02$

$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.56 \text{ e \AA}^{-3}$

Atomic scattering factors
from *International Tables*
for X-ray Crystallography
(1974, Vol. IV)

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

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_j a_i \cdot a_j$			
	x	y	z	B_{eq}
Cu	0.1600 (1)	0.35539 (9)	0.22743 (7)	2.68 (6)
Cl(1)	0.3786 (3)	0.2876 (2)	0.1850 (2)	3.9 (1)
Cl(2)	0.0917 (3)	0.4163 (2)	0.1050 (2)	4.1 (1)
S(1)	0.2733 (4)	0.5141 (3)	0.4023 (2)	4.1 (2)
S(2)	-0.0403 (3)	0.2010 (2)	0.2093 (2)	3.2 (1)
O	-0.080 (2)	0.279 (1)	0.4775 (8)	15 (1)
N(1)	-0.0324 (8)	0.4084 (5)	0.2737 (5)	2.3 (4)
N(2)	0.252 (1)	0.3313 (6)	0.3458 (5)	2.8 (4)
N(3)	0.390 (1)	0.3687 (7)	0.4702 (5)	4.1 (5)
N(4)	-0.228 (1)	0.1313 (6)	0.3195 (5)	3.8 (5)
N(5)	0.029 (1)	0.0694 (6)	0.3136 (5)	3.2 (4)
C(1)	-0.012 (1)	0.4877 (7)	0.3184 (6)	2.5 (5)
C(2)	-0.132 (1)	0.5223 (7)	0.3627 (6)	3.5 (6)
C(3)	-0.274 (1)	0.4766 (8)	0.3618 (7)	3.9 (6)
C(4)	-0.296 (1)	0.3969 (8)	0.3117 (6)	3.4 (5)
C(5)	-0.174 (1)	0.3659 (7)	0.2672 (6)	2.4 (4)
C(6)	0.143 (1)	0.5345 (7)	0.3159 (6)	3.4 (5)
C(7)	0.304 (1)	0.3918 (7)	0.4042 (6)	3.2 (5)
C(8)	0.285 (1)	0.2390 (8)	0.3612 (6)	3.5 (6)
C(9)	0.365 (1)	0.2097 (8)	0.4287 (8)	3.9 (6)
C(10)	0.423 (1)	0.279 (1)	0.4805 (7)	5.1 (7)
C(11)	-0.198 (1)	0.2861 (8)	0.2091 (6)	3.5 (5)
C(12)	-0.087 (1)	0.1262 (7)	0.2910 (6)	2.8 (5)
C(13)	-0.256 (1)	0.069 (1)	0.3793 (8)	5.2 (7)
C(14)	-0.145 (1)	0.0077 (9)	0.4083 (7)	4.4 (7)
C(15)	-0.001 (1)	0.0102 (8)	0.3736 (7)	4.3 (6)
C(16)	0.038 (2)	0.246 (1)	0.5241 (9)	8 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cu—Cl(1)	2.244 (3)	N(1)—C(1)	1.35 (1)
Cu—Cl(2)	2.257 (3)	N(1)—C(5)	1.35 (1)
Cu—N(1)	1.996 (7)	N(2)—C(7)	1.35 (1)
Cu—N(2)	2.108 (8)	N(2)—C(8)	1.35 (1)
Cu—S(2)	2.779 (3)	N(3)—C(7)	1.33 (1)
S(1)—C(6)	1.79 (1)	N(3)—C(10)	1.31 (1)
S(1)—C(7)	1.75 (1)	N(4)—C(12)	1.31 (1)
S(2)—C(11)	1.81 (1)	N(4)—C(13)	1.36 (1)
S(2)—C(12)	1.78 (1)	N(5)—C(12)	1.32 (1)
O—C(16)	1.33 (2)	N(5)—C(15)	1.33 (1)
N(1)—Cu—N(2)	89.0 (3)	C(11)—S(2)—C(12)	101.5 (5)
N(1)—Cu—Cl(1)	174.9 (2)	Cu—N(1)—C(1)	115.8 (6)
N(1)—Cu—Cl(2)	91.2 (2)	Cu—N(1)—C(5)	123.8 (7)
N(1)—Cu—S(2)	79.6 (2)	C(1)—N(1)—C(5)	120.2 (8)
N(2)—Cu—Cl(1)	86.7 (2)	Cu—N(2)—C(7)	131.5 (7)
N(2)—Cu—Cl(2)	165.7 (2)	Cu—N(2)—C(8)	113.3 (7)
N(2)—Cu—S(2)	100.1 (2)	C(7)—N(2)—C(8)	114.5 (9)
Cl(1)—Cu—Cl(2)	93.7 (1)	C(7)—N(3)—C(10)	117 (1)
Cl(1)—Cu—S(2)	98.7 (1)	C(12)—N(4)—C(13)	115 (1)

Cl(2)—Cu—S(2)	94.0 (1)	C(12)—N(5)—C(15)	115 (1)
C(6)—S(1)—C(7)	105.1 (5)		
S(1)—C(6)—C(1)—N(1)	-102.3 (9)	C(1)—C(6)—S(1)—C(7)	61.5 (9)
S(2)—C(11)—C(5)—N(1)	44 (1)	C(5)—C(11)—S(2)—C(12)	83.6 (8)

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed using full-matrix least-squares methods, with non-H atoms anisotropic and H atoms in calculated positions with fixed displacement parameters ($1.2 \times B_{\text{eq}}$ of the carrying atom). Calculations were performed with *TEXSAN* (Molecular Structure Corporation, 1989) software using a VAXstation 3520 computer. The figures were drawn with *ORTEPII* (Johnson, 1976).

RK thanks Suomen Kulttuurirahasto for a grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: AB1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1064–1065

[RuCl₂(PH₂Cy)(η^6 -*p*-cymene)]

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(Received 27 October 1993; accepted 27 January 1994)

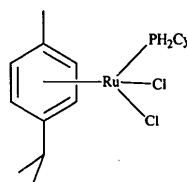
Abstract

The structure of dichloro(cyclohexylphosphine)(η^6 -*p*-cymene)ruthenium, [RuCl₂(η^6 -C₁₀H₁₄)(C₆H₁₃P)], is reported. The structure determination shows that the C

atoms of the aromatic six-membered ring are almost equidistant from the Ru atom, at distances close to the average value of 2.21 (3) Å. The other metal–ligand distances are Ru—P 2.299 (2), Ru—Cl1 2.411 (1) and Ru—Cl2 2.408 (1) Å. The distances and angles for the Ru environment show a pseudo-octahedral coordination in which the phenyl ring occupies three of the corners of the distorted octahedron.

Comment

This work is part of a project dealing with the reactivity of binuclear ruthenium complexes (Cabeza, Mulla & Riera, 1994), as the title compound, (I), is a derivative of [Ru₂Cl₄(η^6 -*p*-cymene)₂]. The angles formed by the centroid



(I)

(CZ) of the *p*-cymene phenyl ring and the other Ru ligands are CZ—Ru—P 131.1 (2), CZ—Ru—Cl1 128.6 (2) and CZ—Ru—Cl2 128.5 (2)°. These values and the bond distances and angles of the title compound are in good agreement with those found in similar compounds (Regragui, Dixneuf, Taylor & Carty, 1984; Cabeza, Mulla & Riera, 1994).

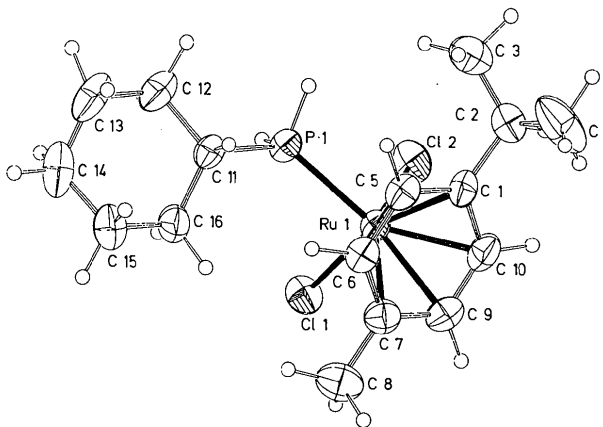


Fig. 1. *EUCLID* (Spek, 1982) plot of the title compound showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The compound was prepared in quantitative yield from [Ru₂Cl₄(η^6 -*p*-cymene)₂] and PH₂Cy following the procedure described for the synthesis of the analogous complex [RuCl₂(PHPh₂)(η^6 -*p*-cymene)] (Regragui, Dixneuf, Taylor & Carty, 1984).