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Absolute Configuration of Di(perchlorato-*O*)tetra(pyridine-*N*)copper(II), [Cu(ClO₄)₂(py)₄]

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Abstract

The crystal of the title complex consists of neutral [Cu(ClO₄)₂(C₅H₅N)₄] units. The two perchlorate ligands occupy the axial positions of a distorted octahedral environment around the metal ion; the axial Cu—O bonds are relatively weak. The absolute configuration has been established; the four pyridine molecules display a right-handed screw arrangement around the Cu^{2+} ion.

Comment

The preparation of the title compound was first reported by Ripan (1924). Papers dealing with magnetic, infrared, electronic absorption and ESR studies, and X-ray data of [Cu(ClO₄)₂(py)₄] and related [CuX₂(py)₄] (py = C₅H₅N; X = BF₄⁻, NO₃⁻, p-CH₃C₆H₄SO₃⁻, CF₃CO₂⁻) began to appear about 30 years later (Ibers, 1953; Brown, Nuttall, McAvoy & Sharp, 1966; Jones & Bull, 1968; Alleyne & Thompson, 1974; Pradilla, Chen, Koknat & Fackler, 1979; Barker & Stobart, 1980; Gowda, Naikar & Reddy, 1984). The only complete structural study was made on tetra(pyridine)bis(trifluoroacetato)-copper(II) (Pradilla, Chen, Koknat & Fackler, 1979). It crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ and the Cu^{II} ion possesses the classic elongated octahedral environment.

The crystal of [Cu(ClO₄)₂(py)₄] (I) used in our study is optically active, consistent with the orthorhombic $P2_12_12_1$ space group. A comparison with

(I)
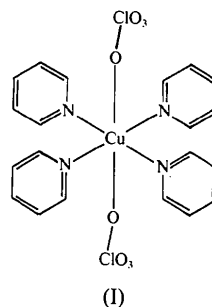
[Cu(BF₄)₂(py)₄] (Ibers, 1953) shows that both crystallize in the same space group with similar cell parameters. These preliminary results and the surprising conclusions of the study of Barker & Stobart (1980) about the Cu stereochemistry, prompted us to perform the determination of the molecular structure of [Cu(ClO₄)₂(py)₄].

The atom-numbering scheme and absolute configuration of [Cu(ClO₄)₂(py)₄] are depicted in Fig. 1. The molecule adopts an elongated octahedral geometry about the Cu atom involving four pyridine N atoms in the equatorial plane and two perchlorate O atoms in axial positions. The Cu—N distances of 2.006 (5)–2.042 (5) Å and the two long Cu—O (perchlorate) distances of 2.476 (7) and 2.559 (6) Å are common for hexacoordinate Cu compounds (Gowda, Naikar & Reddy, 1984). The contacts between neighbouring molecules are normal, the shortest being an O₃ClO···CH distance of 3.04 Å.
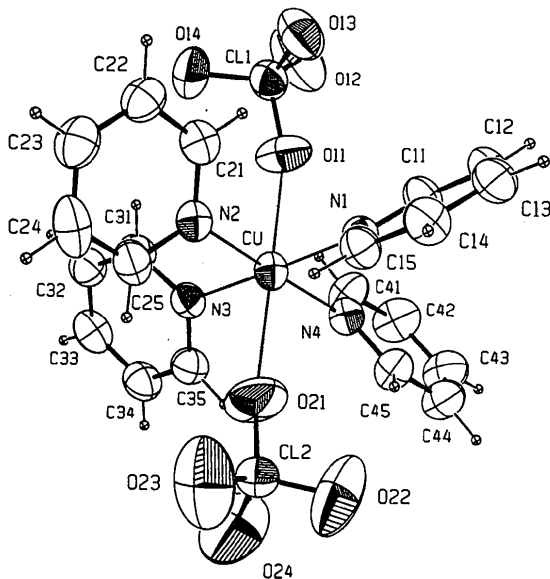

Fig. 1. Molecular geometry and atomic numbering scheme with non-H atoms as principal ellipsoids at the 40% probability level and H atoms as small spheres of arbitrary size.

The values of the dihedral angles between the equatorial plane (containing the Cu and the four N atoms) and the planes of the four aromatic rings are 48.8 (2), 59.2 (2), 44.3 (2) and 57.7 (2)°. This indicates a similar orientation for each ring with respect to the equatorial plane. The right-handed screw arrangement of the four pyridine molecules around the Cu^{2+} ion can be seen clearly in Fig. 1. This confers optical activity to the compound in the solid state, although the ligands are all unidentate. The situation may be the same for $[Cu(BF_4)_2(py)_4]$ (Ibers, 1953), whereas in all other known structures of complexes with the general formula $[MX_2(py)_4]$, where M is a first-row transition-metal ion, both enantiomers are always present in the unit cell (Hamm, Bordner & Schreiner, 1973; Long & Clarke, 1978).

These pyridine complexes are used often as starting materials in reactions involving anhydrous conditions. $[Cu(ClO_4)_2(py)_4]$ and the isomorphous $[Cu(BF_4)_2(py)_4]$ complex may also contribute to enantiomer separation via diastereomeric salt formation.

Experimental

Crystals of $[Cu(ClO_4)_2(py)_4]$ were obtained by slow diffusion of water into an ethanol-dimethyl sulfoxide solution containing copper(II) perchlorate and pyridine.

Crystal data

$[Cu(ClO_4)_2(C_5H_5N)_4]$	Cu $K\alpha$ radiation
$M_r = 578.85$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 10.302$ (1) Å	$\theta = 23-26°$
$b = 13.960$ (1) Å	$\mu = 3.84$ mm^{-1}
$c = 16.640$ (1) Å	$T = 296$ K
$V = 2393.1$ (6) Å^3	Parallelepiped
$Z = 4$	$0.37 \times 0.24 \times 0.20$ mm
$D_x = 1.607$ Mg m^{-3}	Blue

Data collection

Enraf-Nonius CAD-4	$R_{int} = 0.038$
diffractometer	$\theta_{max} = 72°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 12$
Absorption correction:	$k = 0 \rightarrow 17$
empirical	$l = 0 \rightarrow 20$
$T_{min} = 0.92$, $T_{max} = 0.99$	3 standard reflections
2691 measured reflections	frequency: 120 min
2665 independent reflections	intensity variation: 1%
2400 observed reflections	
$[F_o^2 \geq 3\sigma(F_o^2)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.09$
$R = 0.048$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
$wR = 0.047$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
$S = 1.13$	

2400 reflections
316 parameters
H-atom parameters not refined
$w = 1.0$ if $|F_o| < 192.1$ and
$w = (192.1/|F_o|)^2$ if $|F_o| \geq 192.1$

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.26371 (8)	0.26471 (6)	0.25030 (6)	4.21 (2)
Cl1	0.0012 (2)	0.3483 (1)	0.1050 (1)	5.85 (4)
Cl2	0.5031 (2)	0.1689 (2)	0.40739 (9)	4.70 (3)
O11	0.1235 (5)	0.3267 (5)	0.1345 (4)	8.1 (2)
O12	0.006 (1)	0.3843 (5)	0.0278 (3)	11.0 (2)
O13	-0.0564 (6)	0.4198 (4)	0.1609 (4)	8.1 (2)
O14	-0.0734 (6)	0.2620 (4)	0.1097 (5)	9.3 (2)
O21	0.4105 (6)	0.1966 (6)	0.3534 (4)	12.6 (2)
O22	0.5768 (7)	0.2502 (6)	0.4289 (5)	12.4 (2)
O23	0.442 (1)	0.1291 (6)	0.4728 (4)	13.6 (3)
O24	0.5856 (7)	0.1024 (6)	0.3694 (6)	14.8 (3)
N1	0.2551 (5)	0.3940 (3)	0.3067 (3)	4.1 (1)
N2	0.0100 (5)	0.2231 (4)	0.3156 (3)	4.4 (1)
N3	0.2674 (5)	0.1369 (3)	0.1907 (3)	4.2 (1)
N4	0.4181 (5)	0.3114 (4)	0.1863 (3)	4.3 (1)
C11	0.2584 (7)	0.4766 (4)	0.2643 (4)	4.8 (1)
C12	0.2506 (8)	0.5646 (5)	0.3011 (4)	5.6 (2)
C13	0.2422 (8)	0.5711 (5)	0.3831 (4)	5.6 (2)
C14	0.2380 (9)	0.4865 (5)	0.4278 (4)	5.4 (2)
C15	0.2451 (7)	0.3998 (4)	0.3869 (4)	4.5 (1)
C21	-0.0007 (7)	0.2729 (5)	0.3119 (4)	4.8 (1)
C22	-0.1102 (6)	0.2466 (5)	0.3543 (4)	5.2 (2)
C23	-0.1055 (8)	0.1680 (6)	0.4041 (5)	6.0 (2)
C24	0.007 (1)	0.1171 (5)	0.4099 (4)	6.5 (2)
C25	0.1133 (8)	0.1456 (5)	0.3638 (5)	5.5 (2)
C31	0.1579 (7)	0.0993 (5)	0.1616 (4)	4.9 (2)
C32	0.1569 (8)	0.0173 (5)	0.1138 (5)	5.5 (2)
C33	0.2746 (8)	-0.0255 (5)	0.0956 (4)	5.5 (2)
C34	0.3864 (7)	0.0122 (5)	0.1275 (5)	5.6 (2)
C35	0.3808 (7)	0.0933 (5)	0.1755 (4)	5.1 (2)
C41	0.4151 (8)	0.3129 (6)	0.1037 (5)	6.1 (2)
C42	0.5176 (8)	0.3473 (7)	0.0594 (4)	6.7 (2)
C43	0.6284 (8)	0.3806 (6)	0.0993 (5)	6.5 (2)
C44	0.6312 (7)	0.3739 (6)	0.1833 (5)	5.8 (2)
C45	0.5243 (7)	0.3411 (5)	0.2234 (4)	4.9 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu—O11	2.559 (6)	Cu—O21	2.476 (7)
Cu—N1	2.036 (5)	Cu—N2	2.006 (5)
Cu—N3	2.042 (5)	Cu—N4	2.022 (5)
O11—Cu—O21	174.9 (2)	O11—Cu—N1	91.3 (3)
O11—Cu—N2	93.4 (2)	O11—Cu—N3	86.6 (3)
O11—Cu—N4	86.5 (2)	O21—Cu—N1	92.7 (2)
O21—Cu—N2	89.8 (2)	O21—Cu—N3	89.4 (2)
O21—Cu—N4	90.5 (2)	N1—Cu—N2	88.4 (2)
N1—Cu—N3	177.9 (3)	N1—Cu—N4	89.5 (3)
N2—Cu—N3	91.4 (2)	N2—Cu—N4	177.9 (2)
N3—Cu—N4	90.6 (2)		

The structure was solved by direct methods and the full-matrix least-squares refinement used programs of the *SDP* system (B. A. Frenz & Associates, Inc., 1983). The non-H atoms were refined anistropically. H atoms were placed at calculated positions (C—H = 0.95 Å) and their isotropic displacement factors were fixed at approximately 1.1 times the value of the connected atoms. The inversion-related structure was refined in an identical fashion to yield $R = 0.054$, $wR = 0.051$, $S = 1.23$, which is a poorer result than that of the first refinement (Hamilton, 1965). Anomalous-dispersion effects were included in F_c

(Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). The diagram was produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71642 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1052]

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The Monoclinic Phase [Au₂(C₂₅H₂₂P₂)₂]Cl₂.2CH₃CN

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Abstract

Bis[μ-bis(diphenylphosphino)methane-*P,P′*]digold(I) dichloride bis(acetonitrile) solvate, [Au₂(C₂₅H₂₂-P₂)₂]Cl₂.2CH₃CN, crystallized in the monoclinic system. A crystallographic inversion centre lies at the

centre of the molecule. The Au—P distances are 2.299 (3) and 2.332 (3) Å. The Au···Cl distance is 2.951 (4) Å and the Au···Au separation is 2.994 (1) Å. The molecular structure is similar to the previously reported triclinic structure except that a longer Au···Cl distance is observed for the present monoclinic structure.

Comment

In recent years, studies of the metal–metal interactions in the [Au(dppm)*X*]₂ system, where dppm is bis(diphenylphosphino)methane, have increased because of their interesting bonding and luminescent properties (King, Wang, Khan & Fackler, 1989; Khan, King, Heinrich, Fackler & Poter, 1989; Wang, Khan & Fackler, 1989). The structure of [Au(dppm)Cl]₂ solvated with acetone has been reported in the triclinic system (Schmidbauer,
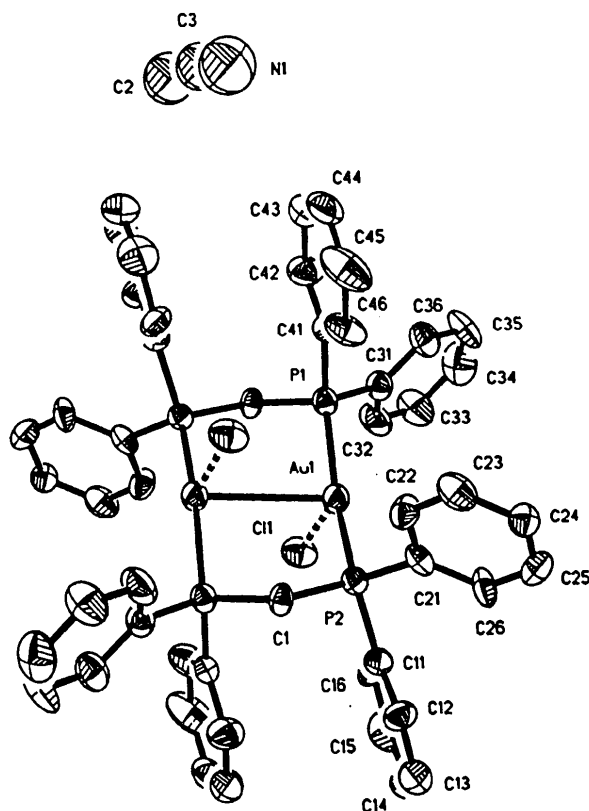

Fig. 1. Molecular drawing of the title compound with 50% probability displacement ellipsoids for the non-H atoms.