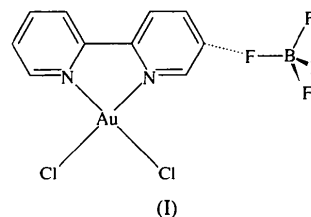


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recrystallized from methanol. A view of the cation in a direction perpendicular to its approximate molecular plane is given in Fig. 1.

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2,2'-Bipyridinedichlorogold(III) Tetrafluoroborate

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Abstract

The crystallographically determined structure of the title compound, $[\text{AuCl}_2(\text{C}_{10}\text{H}_8\text{N}_2)]\text{BF}_4$, is reported. The cation is approximately planar and of C_{2v} local symmetry. Both Au—Cl distances are 2.252 (4) Å and the average Au—N distance is 2.037 (13) Å. One pyridine ring of the bipyridyl ligand is hydrogen bonded to the adjacent BF_4^- anion. There is no significant cation–cation stacking in the solid state.

Comment

The compound (bipy)PtCl₂ (bipy = 2,2'-bipyridine) undergoes a facile 1e reduction to afford the anion [(bipy)PtCl₂][−] in which the platinum oxidation state is formally +1. However, recent work (Macgregor, McInnes, Sorbie & Yellowlees, 1993) has conclusively demonstrated that the lowest unoccupied molecular orbital of the neutral species is bipy-based, and that consequently the anion is correctly formulated as [(bipy[−])Pt^{II}Cl₂]. As a prelude to similar electrochemical studies of the isoelectronic species [(bipy)AuCl₂]⁺, we considered it of importance to establish unequivocally the structure of the cation, particularly in view of the recently suggested possibility of solid-state stacking interactions in the perchlorate salt (Yam, Choi, Lai & Lee, 1993).

The title compound, (I), was synthesized in near quantitative yield by an established procedure and

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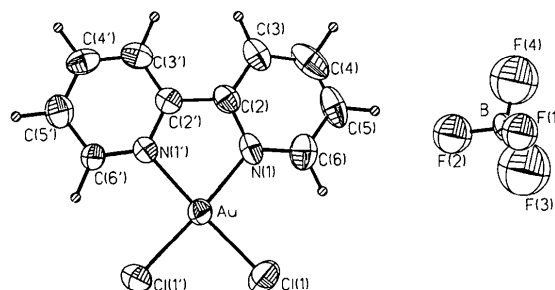


Fig. 1. View of the 2,2'-bipyridinedichlorogold(III) cation and associated tetrafluoroborate anion. 50% probability ellipsoids are shown except for H atoms which are represented by spheres of arbitrary size.

The $[\text{AuN}_2\text{Cl}_2]$ fragment of the cation is approximately planar (maximum atomic deviation from the least-squares plane < 0.05 Å) and the cation as a whole has near C_{2v} local symmetry. While the ring of N(1') is essentially located in this plane [maximum deviation 0.24 Å by C(5')], all the atoms in the N(1) ring lie to one side of the metal coordination plane, with C(3) and C(4) exhibiting the maximum elevation (0.38 Å). It may be of relevance that H(5) is involved in hydrogen bonding to F(2), characterized by C—H...F 2.18 Å, C—H...F 167 and H...F—B 141°.

As far as we are aware, the title compound represents only the second bipyridyl gold(III) species to be crystallographically characterized. The lengths of Au—N(1) and Au—N(1') are not significantly different from each other [average 2.037 (13) Å], but do vary significantly from the average value in [(bipy)Au(mes)₂]⁺ (mes = C₆H₂Me₃-2,4,6) [2.125 (6) Å; Yam, Choi, Lai & Lee, 1993]. This presumably arises from the differing *trans* influences of Cl and mes. The Au—Cl distances in [(bipy)AuCl₂]⁺ are identical [2.252 (4) Å] and the C(2)—C(2') bridge distance is 1.457 (15) Å.

In the crystal, the shortest intermolecular distance between Au atoms is 6.850 Å, *i.e.* the unit-cell repeat in the *a* direction. Clearly this distance does not represent a significant interaction [*cf.* 3.45 and 4.43 Å in the red and yellow forms, respectively, of (bipy)PtCl₂ (Osborn & Rogers, 1974; Herber, Croft, Coyer, Bilash & Sahiner, 1994)]. It is highly probable that [(bipy)AuCl₂]⁺ClO₄[−] and

[(bipy)AuCl₂]₂BF₄ are isomorphous, and highly unlikely that the Au...Au distances in these species will vary much with temperature. In this respect, we consider the possibility of a significant Au...Au stacking interaction in the solid-state structure of [(bipy)AuCl₂]₂ClO₄ at 77 K, recently suggested by Yam, Choi, Lai & Lee (1993), to be somewhat doubtful.

Experimental

The title compound was prepared by a modification of the method of Harris & Lockyer (1959). An aqueous solution of bipy was heated to reflux with a similar solution of Na[AuCl₄] to yield an orange product. Addition of excess HBF₄ precipitated crystals of the target species. Recrystallization from MeOH afforded the title compound as well formed yellow needles in ca 90% yield. Microanalysis: found C 23.52, H 1.64, N 5.47%; C₁₀H₈AuBCl₂F₄N₂ requires C 23.51, H 1.58, N 5.48%. UV/vis (MeCN): ν_{\max} 31 970 cm⁻¹ (ϵ 1.28 × 10⁴ M⁻¹ cm⁻¹).

Crystal data

[AuCl₂(C₁₀H₈N₂)]BF₄

$M_r = 510.83$

Monoclinic

$P2_1/n$

$a = 6.850(4) \text{ \AA}$

$b = 12.852(5) \text{ \AA}$

$c = 15.537(5) \text{ \AA}$

$\beta = 96.33(4)^\circ$

$V = 1359.5(10) \text{ \AA}^3$

$Z = 4$

$D_x = 2.495 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 12\text{--}13^\circ$

$\mu = 11.22 \text{ mm}^{-1}$

$T = 291 \text{ K}$

Needle

$0.3 \times 0.07 \times 0.07 \text{ mm}$

Yellow

$R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 25^\circ$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 18$

2 standard reflections

monitored every 500

reflections

intensity decay: < 1%

Data collection

CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

$T_{\text{min}} = 0.24$, $T_{\text{max}} = 0.50$

2599 measured reflections

2381 independent reflections

2041 observed reflections

$[F > 2\sigma(F)]$

Refinement

Refinement on F

$R = 0.0437$

$wR = 0.0592$

$S = 1.284$

2041 reflections

162 parameters

$w = 1/[\sigma^2(F) + 0.000804F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 2.34 \text{ e \AA}^{-3}$ [near
F(3) and F(4)]

$\Delta\rho_{\text{min}} = -1.34 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV) and

SHELX76 (Sheldrick,

1976)

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

U_{iso} for F atoms; $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ for others.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Au	0.62915 (6)	0.37873 (3)	0.80294 (2)	0.0423 (3)
Cl(1')	0.4107 (5)	0.3801 (3)	0.9011 (2)	0.0665 (19)
Cl(1)	0.8221 (6)	0.4842 (3)	0.8914 (2)	0.078 (2)
N(1)	0.8029 (14)	0.3785 (7)	0.7053 (6)	0.048 (5)
N(1')	0.4660 (12)	0.2821 (6)	0.7186 (5)	0.038 (4)
C(6')	0.3120 (16)	0.2297 (9)	0.7370 (7)	0.047 (6)
C(2')	0.5391 (14)	0.2727 (8)	0.6421 (6)	0.040 (5)
C(3')	0.4421 (18)	0.2107 (9)	0.5776 (7)	0.053 (7)
C(4)	0.991 (2)	0.3819 (13)	0.5625 (10)	0.081 (10)
C(3)	0.8157 (18)	0.3297 (10)	0.5585 (8)	0.058 (7)
C(5')	0.210 (2)	0.1642 (10)	0.6745 (8)	0.061 (8)
C(6)	0.9707 (19)	0.4311 (11)	0.7034 (9)	0.065 (8)
C(4')	0.2813 (19)	0.1561 (9)	0.5954 (7)	0.055 (7)
C(2)	0.7200 (16)	0.3287 (9)	0.6318 (7)	0.047 (6)
C(5)	1.071 (2)	0.4315 (12)	0.6308 (11)	0.074 (9)
F(1)	1.4949 (12)	0.7176 (7)	0.6230 (5)	0.083 (2)
F(2)	1.4932 (15)	0.5480 (9)	0.6609 (6)	0.106 (3)
B	1.6011 (18)	0.6305 (10)	0.6359 (8)	0.046 (7)
F(3)	1.737 (3)	0.6398 (13)	0.7064 (12)	0.200 (7)
F(4)	1.659 (2)	0.5979 (11)	0.5620 (11)	0.165 (6)

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

Au—Cl(1')	2.252 (4)	C(3')—C(4')	1.360 (16)
Au—Cl(1)	2.252 (4)	C(4)—C(3)	1.37 (2)
Au—N(1)	2.028 (10)	C(4)—C(5)	1.30 (2)
Au—N(1')	2.046 (8)	C(3)—C(2)	1.374 (17)
N(1)—C(6)	1.337 (17)	C(5')—C(4')	1.375 (17)
N(1)—C(2)	1.377 (14)	C(6)—C(5)	1.38 (2)
N(1')—C(6')	1.309 (14)	F(1)—B	1.337 (15)
N(1')—C(2')	1.345 (13)	F(2)—B	1.373 (16)
C(6')—C(5')	1.410 (17)	B—F(3)	1.36 (2)
C(2')—C(3')	1.391 (15)	B—F(4)	1.32 (2)
C(2')—C(2)	1.457 (15)		
Cl(1')—Au—Cl(1)	88.35 (13)	C(2')—C(3')—C(4')	118.8 (10)
Cl(1')—Au—N(1)	174.3 (3)	C(3)—C(4)—C(5)	124.0 (15)
Cl(1')—Au—N(1')	94.7 (2)	C(4)—C(3)—C(2)	117.6 (12)
Cl(1)—Au—N(1)	95.9 (3)	C(6')—C(5')—C(4')	117.7 (11)
Cl(1)—Au—N(1')	176.9 (2)	N(1)—C(6)—C(5)	121.7 (13)
N(1)—Au—N(1')	81.1 (4)	C(3')—C(4')—C(5')	121.1 (11)
Au—N(1)—C(6)	126.4 (9)	N(1)—C(2)—C(2')	114.6 (9)
Au—N(1)—C(2)	113.5 (7)	N(1)—C(2)—C(3)	119.5 (10)
C(6)—N(1)—C(2)	119.5 (10)	C(2')—C(2)—C(3)	125.8 (10)
Au—N(1')—C(6')	124.6 (7)	C(4)—C(5)—C(6)	117.6 (14)
Au—N(1')—C(2')	112.9 (6)	F(1)—B—F(2)	112.8 (11)
C(6')—N(1')—C(2')	122.4 (9)	F(1)—B—F(3)	111.0 (13)
N(1')—C(6')—C(5')	120.3 (10)	F(1)—B—F(4)	110.2 (12)
N(1')—C(2')—C(3')	119.6 (9)	F(2)—B—F(3)	100.4 (12)
N(1')—C(2')—C(2)	117.2 (9)	F(2)—B—F(4)	102.9 (12)
C(3')—C(2')—C(2)	123.2 (9)	F(3)—B—F(4)	118.9 (14)

Bipyridine H atoms were set in idealized positions and allowed to ride on their respective C atoms, with C—H = 1.08 \AA . Au, Cl, C, N and B atoms were refined with anisotropic displacement parameters while F atoms were refined isotropically. A single (isotropic) displacement parameter for all H atoms was refined [0.090(16) \AA^2 at convergence].

Structure solution (Patterson and difference Fourier syntheses) and refinement was via *SHELX76* (Sheldrick, 1976). Other programs included *CADABS* (Gould & Smith, 1986), *CALC* (Gould & Taylor, 1986) and *SHELXTL/PC* (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Benzenesulfonylglycylglycine, (I), and Tetrakis(μ -*N*-benzenesulfonylglycylglycinato)bis[aquacopper(II)](*Cu*—*Cu*)—Water (1/4), (II)

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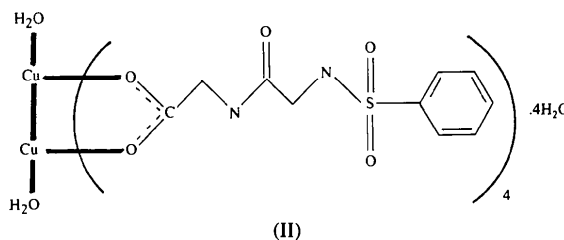
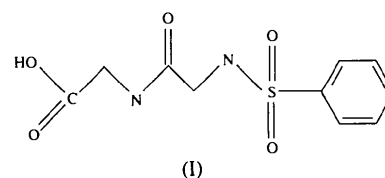
Abstract

Each Cu^{II} ion in $[\{\text{Cu}(\text{H}_2\text{O})\}_2(\mu\text{-C}_{10}\text{H}_{11}\text{N}_2\text{O}_5\text{S})_4]\cdot 4\text{H}_2\text{O}$, (II), is coordinated to its centrosymmetric counterpart, the equatorial carbonyl and carboxylic O atoms of two *N*-benzenesulfonylglycylglycinato moieties and their centrosymmetric counterparts and to an axial water O atom. The centrosymmetrically related Cu^{II} ions

are linked by bridges of 2.641 (1) Å to form dimeric dinuclear units. In both (I) ($\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_5\text{S}$) and (II), the terminal and peptide N atoms are in *cis* conformation. The carboxylic group is localized in (I) but a complete delocalization of this group has been observed in the metal complex. When coordinated by the metal ion, the *N*-benzenesulfonylglycylglycine moieties undergo major conformational changes about the N—C α bonds along the peptide backbone.

Comment

Transition metal complexes of amino acids and peptides are of considerable importance because they provide simple models for more complex metal–enzyme and metal–peptide systems. The crystal structures of (I) and (II) have been determined in order to study the effect of a modified amino acid side chain on the coordinating properties of the peptide bond.



In both (I) and (II), the S—N distances are shorter than the corresponding single-bond distance of 1.764 Å in sulfamic acid (Sass, 1960), indicating considerable double-bond character of the bonds. This shortening is more pronounced in the metal complex; a similar finding has been observed in the structure of *N*-benzenesulfonyl-DL-alanine and its copper complex (Chaudhuri, 1984). The enlargement of the S—O bond distances in the metal complex may be due to the increased double-bond character of the S—N(1) bonds in the complex.

The N(1)—C(7) bond distances in both of the structures are shorter than corresponding distances measured in α -glycylglycine [1.484 (2) Å reported by Kvick, Al-Karaghoulis & Koetzle (1977), and 1.497 Å by Biswas, Hughes, Sharma & Wilson (1968)]. Shortening of the N(1)—C(7) bond may be attributed to the conjugation of the benzene sulfonamide group with the glycylglycine moiety. The carbonyl group [C(8)—O(3)] is delocalized in both the free ligand and the complex. The terminal and peptide N atoms are in *cis* conformation in both the free ligand (I) and the complex (II).