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Crystal and Molecular Structure of Dichloro(ethylenediamine)gold(III) Nitrate: [Au(NH₂CH₂CH₂NH₂)Cl₂]NO₃

D. Michelle Motley,

Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA

Judith A. Walmsley,

Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA

Julio Zukerman-Schpector, and

Department of Chemistry, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil

Edward R. T. Tiekink

Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA

Judith A. Walmsley: Judith.Walmsley@utsa.edu; Edward R. T. Tiekink: Edward.Tiekink@utsa.edu

Abstract

The gold(III) atom in [Au(NH₂CH₂CH₂NH₂) Cl₂]NO₃ is chelated by the ethylenediamine (en) ligand and the approximately square planar geometry is completed by two chloride atoms. Weak Au...O and Au...Cl contacts are noted above and below the square plane leading to a tetragonally distorted octahedron for the gold(III) center. Extensive charge-assisted hydrogen bonding of the type N–H...O leads to the formation of a 2-D array and layers are consolidated into a 3-D network via C–H...O and C–H...Cl contacts. The compound crystallizes in the orthorhombic space group *Pbca* with *a* = 10.3380(11) Å, *b* = 8.2105(7) Å, *c* = 19.625(2) Å, and *Z* = 8.

Keywords

Gold; Ethylenediamine; Hydrogen bonding; Charge-assisted hydrogen bonding

Introduction

Gold compounds have a long history in medicine, being employed by Arabic, Chinese and Indian physicians for thousands of years [1, 2]. In contemporary times, gold compounds such as Myocrisin[®], a polymeric, charged and water-soluble sodium aurothiomalate, and Auranofin[®], a mononuclear, lipophilic triethylphosphinegold(I) tetra-acetylated thioglucose

species, both Disease Modifying Anti-Rheumatic Drugs (DMARDs), are used in the treatment of extreme forms of rheumatoid arthritis [1, 2] (Fig. 1). In order to expand *chrysotherapy*, which is the use of gold in medicine, other potential applications of gold compounds have been explored, such as for the treatment of human immunodeficiency virus (HIV), bronchial asthma, malaria and Chagas disease [3]. Arguably, most attention in this context relates to the development of novel anti-tumor agents [4–6]. While considerable effort has been devoted to exploring the anti-proliferative efficacy of gold(I) species, more recent attention, and success, has been found for gold(III) species [5, 6]. Motivation for the study of gold(III) species arises to a large extent owing to the similarity anticipated for these d^8 systems and those of well known anti-cancer drugs such as cisplatin, i.e., *cis*-diaminedichloroplatinum(II), and second generation platinum(II) species [7].

A favored mechanism of action proposed to explain the anti-cancer activity of cisplatin is its interaction with the nucleobases of intracellular DNA [7]. In this context, our interest in gold(III) complexes related to the title complex concerns the investigation of the interaction of gold(III) species with nucleobases such as guanosine 5'-monophosphate [8]. The title complex, $[\text{Au}(\text{en})\text{Cl}_2]\text{NO}_3$, en = 1,2-diaminoethane, was prepared during an attempt to replace all of the chloro ligands of $[\text{Au}(\text{en})\text{Cl}_2]\text{Cl}$ in ethanolic solution. The motivation was to replace the chloro ligands with ethanol or nitrate ligands, and for the anion to be nitrate, to provide a complex with more labile ligands in order facilitate complexation studies of gold(III) with nucleotides such as guanosine 5'-monophosphate [8]. Herein, full characterization of $[\text{Au}(\text{en})\text{Cl}_2]\text{NO}_3$ by single crystal X-ray crystallography is reported.

Experimental

Synthesis

$\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ (0.564 g, 1.42 mmol) was dissolved in absolute ethanol (20 mL) and ethylenediamine (94.7 μL , 1.42 mmol) was added. After heating and stirring the solution for 45 min, three molar equivalents AgNO_3 (0.7144 g, 4.206 mmol) was added to the resulting yellow solution. After an additional 30 min of heating, the warm solution was a pale green-yellow color with a AgCl precipitate. The mixture was cooled and filtered twice to ensure maximum removal of the AgCl precipitate. The filtrate was evaporated to dryness and the solid was washed once with cold EtOH. Yield: 0.447 g (79%). Elemental analysis. Calculated for $[\text{Au}(\text{en})\text{Cl}_2]\text{NO}_3$: C, 6.16; H, 2.07; N, 10.78. Found: C, 5.58; H, 1.69; N, 10.40.

The crystal for the X-ray structure determination was grown by vapor diffusion of diethyl ether into an acetonitrile solution of the compound.

X-ray Crystallography

Intensity data for a yellow crystal of $[\text{Au}(\text{en})\text{Cl}_2]\text{NO}_3$ were collected at 93 K on a Rigaku AFC12/Saturn724 CCD fitted with Mo $K\alpha$ radiation. The data set was corrected for absorption based on multiple scans [9] and reduced using standard methods [10]. The structure was solved by heavy-atom methods with SHELXS-97 [11] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-97 [11] with anisotropic displacement

parameters for non-hydrogen atoms, hydrogen atoms in their calculated positions and a weighting scheme of the form $w=1/[\sigma^2(F_o^2)+(0.080P)^2+8.721P]$ where $P=(F_o^2+2F_c^2)/3$. The maximum residual electron density peak of 2.35 e Å⁻³ was located 1.07 Å from the Au atom. Crystal data and refinement details are given in Table 1. Figure 2, showing the atom labeling scheme, was drawn with 50% displacement ellipsoids using ORTEP [12] and the remaining figures were drawn with DIAMOND [13]. Data manipulation and interpretation were accomplished using teXsan [14] and PLATON [15].

Results and Discussion

The original purpose of the reaction leading to the formation of [Au(en)Cl₂]NO₃ was the preparation of a Au(III) complex in non-aqueous solution in which the ligands would be more easily substituted than the chloro ligands. However, the conditions were not sufficiently rigorous and only the chloride anion was replaced by nitrate. Full characterization of the resulting complex was afforded by X-ray crystallography.

The molecular structure of [Au(en)Cl₂]NO₃ is shown in Fig. 2 and selected geometric parameters are collected in Table 2. The Au atom is coordinated by a chelating ethylenediamine ligand and two chlorides that define a Cl₂N₂ donor set and a square planar geometry. The deviations of the Cl1, Cl2, N1, and N2 atoms from their least-squares plane are 0.059(2), -0.061(2), 0.073(2), and -0.072(2) Å, respectively, with the Au atom lying -0.031(2) Å out of this plane. The greatest deviation from the ideal square planar geometry is attributed to the acute angle formed by the five-membered chelate ring. The conformation of the en ring is an envelope on C2. The Au-Cl and Au-N bond distances observed in the structure of [Au(en)Cl₂]NO₃ resemble those found in the two most closely related literature structures, namely [Au(en)Cl₂]Cl · 2H₂O [8] and [Au(2,2'-bipyridine)Cl₂]NO₃ [16]. In the latter structure, close Au···O(nitrate) interactions of 3.008(5) Å are noted above and below the AuCl₂N₂ square plane; the cation has crystallographic two-fold symmetry. In the present structure, a similar Au···O(nitrate)ⁱ contact of 2.999(5) Å is found (symmetry operation i: ½ - x, -½ + y, z). Such close Au···O contacts are well known in gold chemistry, but are not considered to represent significant bonding interactions [17–19]. In the same vein, a weak intermolecular Au···Cl₂ⁱⁱ contact of 3.3132(17) Å is found, ii: ½ - x, ½ + y, z. The loosely connected O1ⁱ and Cl₂ⁱⁱ atoms subtend an angle of 156.5(1)° at the gold atom so that taken to the extreme, the coordination geometry for gold may be described as a tetragonally distorted octahedron based on a Cl₃N₂O donor set. The presence of the close Au···Cl₂ⁱⁱ interaction is the likely explanation for the marginal elongation of the Au-Cl₂ bond distance compared with the Au-Cl₁ bond, Table 2.

There is a considerable number of charge-assisted hydrogen bonding interactions involving amine-H and nitrate-O atoms; geometric parameters describing these are collected in Table 3. The three strongest N-H···O charge-assisted hydrogen bonding interactions operating in the crystal structure of [Au(en)Cl₂]NO₃, judged on distance considerations, connect ions into a two-dimensional array, as highlighted in Fig. 3. The O1 atom participates in two N-H···O contacts and the O2 atom forms only one N-H···O contact, which are shown as orange dashed bonds in Fig. 3; the O2 also forms a weak Au···O2 interaction in this plane (see above). The O3 atom forms only one significant intermolecular interaction and that is with

N2. This interaction is considerably longer (2.46 Å) compared with those formed by the other nitrate-O atoms, i.e., N–H···O at 1.98–2.03 Å, shown as blue-dashed lines in Fig. 3. The connections between the nitrate-O1 and amine-N1 groups lead to the formation of chains along the *b*-axis and these are linked into a layer via the N2–H4 μ ···O2 hydrogen bonds. Additional stability to the layer is afforded by the aforementioned weaker N2–H4 μ ···O3 interactions. In terms of hydrogen-bonded rings, kinked chains of dissymmetric 12-membered {···HNH···ONO···HNAuNH···O} rings are formed along the *b*-axis and these are connected laterally, along the *c*-axis, via a chain of alternating centrosymmetric 16-membered {···HNAuNH···ONO}₂ and centrosymmetric 12-membered {···HNH···ONO}₂ rings. The presence of C–H···O, N–H···Cl, and C–H···Cl interactions as well as the aforementioned weak Au···Cl contacts, connect the layers into a consolidated three-dimensional array, Fig. 4.

Acknowledgments

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Fig. 1.

Chemical structures for representative contemporary gold drugs **(1)** the polymeric, charged and water-soluble sodium aurothiomalate (Myocrisin®) and **(2)** the mononuclear, lipophilic triethylphosphinegold(I) tetraacetylated thioglucose species (Auranofin®)

Fig. 2. Molecular structure of [Au(en)Cl₂]⁺NO₃⁻ showing the atom labeling scheme and highlighting the closest hydrogen bonding contact between the ions (black dashed line). Displacement ellipsoids are drawn at 50% probability level

Fig. 3.

A view of the two-dimensional array in [Au(en)Cl₂]⁺NO₃⁻ mediated by charge-assisted N–H...O hydrogen bonding shown as orange- and blue-dashed bonds (see text). Color code: gold, orange; chloride, cyan; oxygen, red; nitrogen, blue; carbon, grey; hydrogen, green

Fig. 4.

A view down the c -axis showing the global crystal packing, i.e., the stacking of layers, in $[\text{Au}(\text{en})\text{Cl}_2]\text{NO}_3$. Hydrogen bonding interactions are shown as orange dashed lines. Color code: gold, orange; chloride, cyan; oxygen, red; nitrogen, blue; carbon, grey; hydrogen, green

Table 1Crystal data and refinement details for [Au(en)Cl₂]₂NO₃

Empirical formula	C ₂ H ₈ AuCl ₂ N ₃ O ₃
Formula weight	389.98
Crystal habit, color	Plate, yellow
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	10.3380(11)
<i>b</i> (Å)	8.2105(7)
<i>c</i> (Å)	19.625(2)
Volume (Å ³)	1665.7(3)
<i>Z</i>	8
Density (calculated, g cm ⁻³)	3.110
Absorption coefficient (mm ⁻¹)	18.270
Transmission factors	0.315–1.000
<i>R</i> (000)	1424
Crystal size (mm)	0.05 × 0.10 × 0.20
θ range for data collection (°)	2.9–25.5
Reflections collected	11418
Independent reflections	1501
<i>R</i> _{int}	0.045
Reflections with <i>I</i> ≥ 2σ(<i>I</i>)	1484
Number of parameters	100
Goodness-of-fit on <i>F</i> ²	1.17
<i>a</i> , <i>b</i> for weighting scheme	0.080, 8.721
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> 1 = 0.041, <i>wR</i> 2 = 0.120
<i>R</i> indices [all data]	<i>R</i> 1 = 0.041, <i>wR</i> 2 = 0.121
Largest difference	
Peak and hole (Å ⁻³)	2.35, −2.54
CCDC deposition no.	691683

Table 2Selected bond lengths (Å) and angles (°) for [Au(en)Cl₂]⁺NO₃⁻

Au–Cl1	2.2668(17)	Au–Cl2	2.2834(16)
Au–N1	2.032(6)	Au–N2	2.046(5)
N3–O1	1.267(7)	N3–O2	1.254(7)
N3–O3	1.237(8)		
Cl1–Au–Cl2	92.06(7)	Cl1–Au–N1	174.12(16)
Cl1–Au–N2	93.32(15)	Cl2–Au–N1	90.75(16)
Cl2–Au–N2	174.34(15)	N1–Au–N2	84.0(2)

Table 3

Hydrogen bonding parameters (A–H...B; Å, °) for [Au(en)Cl₂][NO₃]

A	H	B	H...B	A...B	A–H...B	Symmetry operation
N1	H1 <i>n</i>	O1	1.97	2.846(7)	158	$\frac{1}{2} - x, -\frac{1}{2} + y, z$
N1	H2 <i>n</i>	O1	1.96	2.835(7)	159	$\frac{1}{2} + x, y, \frac{1}{2} - z$
N2	H3 <i>n</i>	Cl1	2.61	3.422(6)	147	$\frac{1}{2} - x, \frac{1}{2} + y, z$
N2	H4 <i>n</i>	O3	2.45	3.116(8)	129	$\frac{1}{2} - x, \frac{1}{2} + y, z$
N2	H4 <i>n</i>	O2	2.01	2.929(7)	172	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
C2	H2 <i>a</i>	O2	2.52	3.238(8)	130	$\frac{1}{2} - x, -\frac{1}{2} + y, z$
C2	H2 <i>b</i>	Cl1	2.61	3.380(8)	134	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
C2	H2 <i>b</i>	O3	2.52	3.040(8)	112	$\frac{1}{2} - x, \frac{1}{2} + y, z$