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New Stable Complexes of Au(III) with Biuret: X-ray Structure of *cis*-[Au(Biu)Br₂]PPh₄ and *Ab Initio* Investigation of *cis*-[Au(Biu)X₂]⁻

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NEW STABLE COMPLEXES OF Au(III) WITH BIURET: X-RAY STRUCTURE OF *cis*-[Au(Biu)Br₂]PPh₄ AND *AB INITIO* INVESTIGATION OF *cis*-[Au(Biu)X₂][−]

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Two anionic complexes of Au(III) with the bioligand biuret, *cis*-[Au(Biu)X₂][−] (BiuH₂ = biuret, X = Cl, Br), have been synthesized and characterized. The molecular structure of *cis*-[Au(Biu)Br₂]PPh₄ has been determined by X-ray diffraction analysis. The complex anion has square-planar geometry with one deprotonated biuret dianion coordinated bidentately to the metal center via the terminal amino nitrogen atoms and two bromide ions in *cis* positions. There are no significant intermolecular Au–Au interactions in the solid state. *Ab initio* calculations of the geometric structure at different computational levels for biuret and both anionic complexes as well an IR study of the structures obtained are performed.

Keywords: Au(III) complexes; Biuret; X-ray data; *Ab initio* calculations; IR study

INTRODUCTION

During the last two decades the synthesis, structure and physiological activity of Au(III) complexes have been studied due to their close similarity in structure to Pt(II) complexes. The biological and therapeutic applications, including antitumor activity of some Au(III) complexes, are already well documented [1–5]. It is generally supposed that therapeutic action and especially antitumor activity is due to direct interaction with DNA. The Au(III) binding on DNA has been studied using both spectroscopic and X-ray methods and the coordination is similar to the isoelectronic Pt(II) ions [6–9]. However, Au(III) complexes are rather unstable, easily undergoing hydrolysis and further reduction to Au(I). For this reason the synthesis and investigation of new Au(III) complexes and especially of *cis*-Au^{III}LX₂ (X = Cl[−], Br[−], I[−]) is of importance.

Biuret (H₂N–CO–NH–CO–NH₂) (BiuH₂) is a good ligand for complexes of this type. As a bioligand it is nontoxic, and its capability (especially in its doubly deprotonated

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form) to stabilize high oxidation states (Cu(III), Pd(III), Pt(III) as “Platinum Blues”, etc) is already proven [10–14]. The aim of the present study was to obtain new complexes of the type *cis*-Au^{III}(Biu)X₂ with potential physiological activity.

EXPERIMENTAL

Synthetic Procedures

90 mg (0.225 mmol) of NaAuCl₄ (Aldrich) and 348 mg (3.38 mmol) of biuret (Merck) (M:L=1:15) were mixed in water at ambient temperature and constant stirring. After 24 h a methanol solution of 234 mg (0.56 mmol) tetraphenylarsonium chloride (Ph₄AsCl) or 236 mg (0.56 mmol) tetraphenylphosphonium bromide (Ph₄PBr) were added and the yellow residues formed were filtered, washed repeatedly with distilled water and dried over P₄O₁₀ for 2 weeks. Yields are 53 and 67%, respectively.

Anal. Calcd. for [Au(Biu)Br₂]Ph₄P (**1**) (%): C, 39.2; H, 2.9; N, 5.3; Br, 20.1. Found: C, 38.7; H, 3.0; N, 5.5; Br, 20.5. ¹H NMR (300 MHz, CDCl₃): δ 7.93 (t, 4H, C₆H₅-*p*), 7.79 (td, 8H, ¹J(HH)=8 Hz, ²J(HH)=3.6 Hz, C₆H₅-*m*), 7.64 (dd, 8H, ¹J(HH)=7.5 Hz, ²J(PH)=13 Hz, C₆H₅-*o*), 2.17 (s, 1H, NH_{middle}), 1.25 (s, 2H, NH_{coordinated}).

Anal. Calcd. for [Au(Biu)Cl₂]Ph₄As (**2**) (%): C, 41.5; H, 3.1; N, 5.6; Cl, 9.4. Found: C, 41.4; H, 3.2; N, 5.8; Cl, 9.8. ¹H NMR (300 MHz, CDCl₃): δ 7.89 (t, 4H, ¹J(HH)=8 Hz, C₆H₅-*p*), 7.78 (t, 8H, ¹J(HH)=8 Hz, C₆H₅-*m*), 7.63 (d, 8H, ¹J(HH)=8 Hz, C₆H₅-*o*), 1.25 (s, 2H, NH_{coordinated}).

Both complexes are soluble in organic solvents (CHCl₃, CH₂Cl₂, acetone).

The [Au(Biu)Br₂]Ph₄P was recrystallized from CHCl₃–hexane solution resulting in yellow needles suitable for X-ray analysis.

Physical Measurements

The solid state IR spectra were recorded on a Bruker IFS-113 FT-IR spectrometer (KBr and CsI disks in spectral ranges 4000–400 and 400–150 cm⁻¹, respectively). The ¹H NMR spectra (solvent CDCl₃) were obtained on a Varian 300 NMR spectrometer (external standard Si(CH₃)₄). The X-ray analysis was performed on a Rigaku AFC7R diffractometer. A crystal of **1** was mounted in a glass capillary tube. Data were collected at 23°C on a Rigaku AFC7R automated four-circle diffractometer equipped with monochromated Mo-Kα radiation (λ=0.71069 Å). Calculations were carried out using a program package teXsan for Windows. The structure was solved by the heavy-atom Patterson method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table I.

Quantum-Chemical Calculations

Structure optimizations for biuret and its anionic Au(III) complexes were performed at the *ab initio* RHF level. The geometry optimizations of the structures investigated were done without symmetry restrictions. The calculations described herein were carried out

TABLE I Crystallographic and refinement data for the complex $[\text{Au}(\text{Biu})\text{Br}_2]\text{Ph}_4\text{P}$

Empirical formula	$[\text{AuC}_2\text{O}_2\text{N}_3\text{H}_3\text{Br}_2] \cdot [\text{C}_{24}\text{H}_{20}\text{P}]$
Formula weight	797.23
Crystal color, habit	yellow, prismatic
Crystal dimensions (mm)	$0.25 \times 0.20 \times 0.05$
Crystal system	orthorhombic
Space group	$P_{\text{bca}}(\#61)$
Unit cell parameters: $a(\text{\AA})$	23.098(9)
$b(\text{\AA})$	32.009(7)
$c(\text{\AA})$	6.903(7)
Volume (\AA^3)	5104(4)
Z	8
Calculated density (g cm^{-3})	2.075
$F(000)$	3040
$\mu(\text{Mo-K}\alpha)$ (cm^{-1})	90.19
Temperature ($^\circ\text{C}$)	23
Measured reflections	6579
Structure solution	Patterson Method (DIRDIF92 PATTY)
Refinement method	Full-matrix least-squares on F
No. observations ($I > 3.00\sigma(I)$)	2504
No. variables	316
Reflection/Parameter ratio	7.92
Residuals: R ; R_w	0.071; 0.073
Goodness of fit indicator	2.49

with the MIDI basis set [15] and with the Stewens–Basch–Krauss–Jasien effective core potentials (ECP) and their concomitant basis sets for all the atoms (ECP-31G) [16,17]. Polarization functions on all heavy atoms from ECP-31G and MIDI basis sets were also added. Vibrational analysis of the obtained structures was carried out and the calculated wavenumbers of all normal modes were scaled by a factor of 0.893. The *ab initio* calculations were performed using the GAMESS program package [18].

RESULTS AND DISCUSSION

The reaction of AuCl_4^- with excess biuret results in formation of $[\text{Au}(\text{Biu})\text{Cl}_2]^-$, which is stable in water and air. Potentiometric measurements showed a significant increase of reaction mixture acidity (the initial pH of 4.5 changed to pH 2 after 24 h) due to double deprotonation of the ligand.

The anionic complex could be precipitated with Ph_4AsCl or Ph_4PBr . In the first case yellow $[\text{Au}(\text{Biu})\text{Cl}_2]\text{Ph}_4\text{As}$ is formed. When precipitation is carried out with Ph_4PBr first substitution of Cl^- by Br^- occurs followed by precipitation (Scheme 1). The substitution of Cl^- with Br^- is due most likely to the higher polarizability of the latter resulting in formation of a more stable complex [2].

The molecular structure of $[\text{Au}(\text{Biu})\text{Br}_2]\text{Ph}_4\text{P}$ is shown in Fig. 1. The complexes are square planar, with Br^- ions in *cis* position. The other two coordination sites are occupied by the deprotonated terminal NH groups of biuret. The anionic complex is neutralized with the bulky counterion $[\text{PPh}_4]^+$.

The most important bond lengths and bond angles of the complex are given in Table II. The Au–N bond distances (1.91–2.02 Å) are typical of those for N-donor containing Au(III) complexes [19–23], the Au(III)–Br bond lengths are similar to those of other reported Au–Br bonds [22]. The angles Br1–Au–N2 and Br2–Au–N1 in the

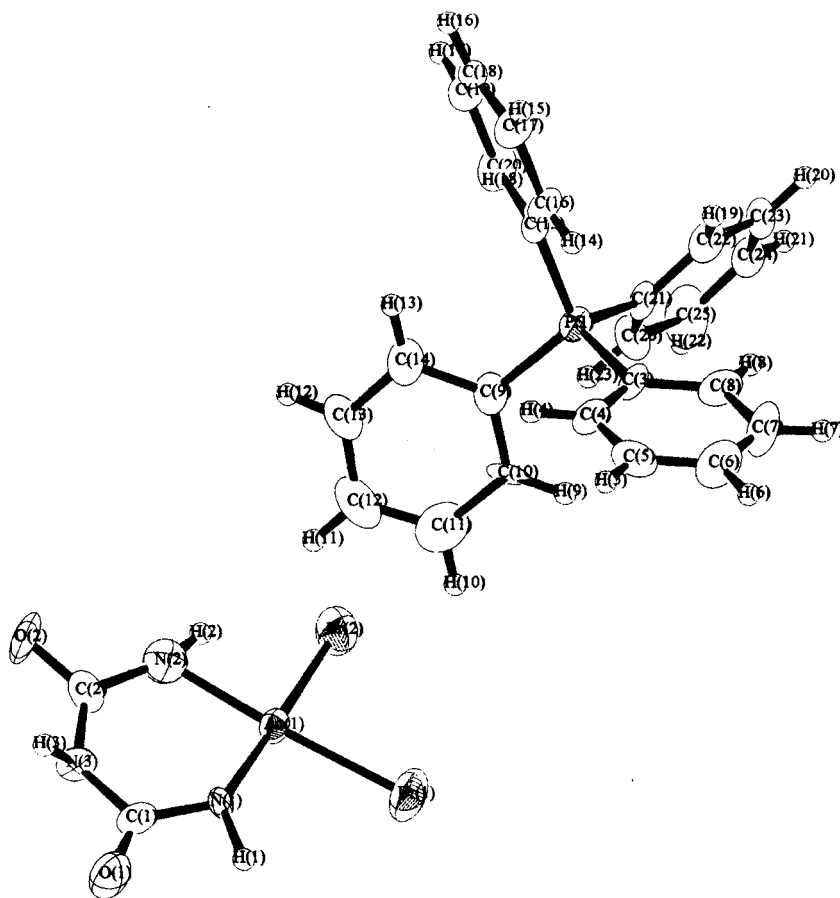
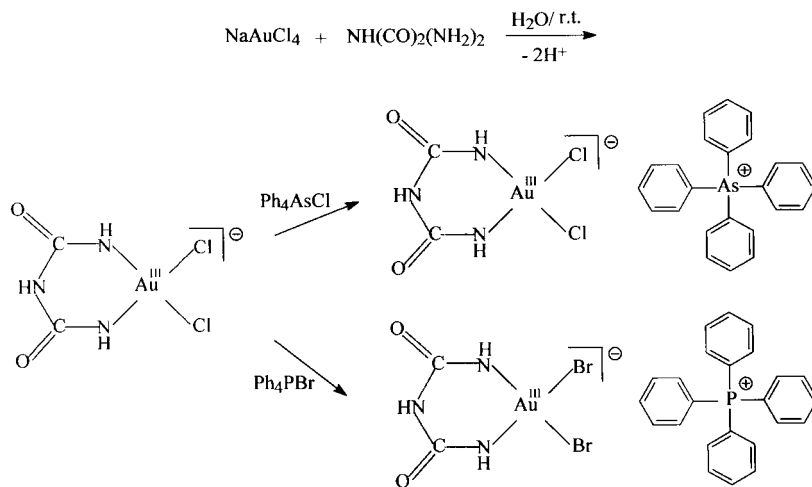


FIGURE 1 Molecular structure of *cis*-[Au(Biu)Br₂]PPh₄.

TABLE II *Ab initio* calculated structure parameters for the $[\text{Au}(\text{Biu})\text{Br}_2]^-$ and $[\text{Au}(\text{Biu})\text{Cl}_2]^-$ complexes and biuret. Bond lengths are in Å and bond angles in degrees. For numbering of the atoms see Fig. 1. The X-ray data for *cis*- $[\text{Au}(\text{Biu})\text{Br}_2]\text{PPh}_4$ are given for comparison

Parameter	$[\text{Au}(\text{Biu})\text{Br}_2]^-$					$[\text{Au}(\text{Biu})\text{Cl}_2]^-$	Biuret
	X-ray	ECP-31G	ECP-31G(d)	MIDI	MIDI(d)	ECP-31G(d)	ECP-31G(d)
<i>Bond</i>							
N1–C1	1.37 (3)	1.3548	1.3475	1.3401	1.3429	1.3472	1.3378
C1–N3	1.39 (3)	1.3972	1.3931	1.3863	1.3893	1.3936	1.4021
N3–C2	1.34 (3)	1.3974	1.3932	1.3862	1.3892	1.3936	1.4021
C2–N2	1.49 (3)	1.3548	1.3476	1.3403	1.3430	1.3472	1.3378
C1–O1	1.21 (3)	1.2582	1.2251	1.2348	1.2061	1.2249	1.2374
C2–O2	1.29 (3)	1.2582	1.2251	1.2348	1.2061	1.2248	1.2374
N1–Au	1.91 (2)	1.9971	1.9957	2.0293	2.0457	1.9855	
N2–Au	2.02 (2)	1.9972	1.9957	2.0293	2.0457	1.9856	
Au–Br1	2.423 (3)	2.5137	2.4867	2.5868	2.5239	2.3546	
Au–Br2	2.413 (4)	2.5136	2.4867	2.5868	2.5239	2.3546	
<i>Bond angle</i>							
C2–N3–C1	130 (3)	132.3	133.2	133.9	134.8	133.2	134.3
O1–C1–N3	116 (3)	117.7	118.0	118.3	118.5	118.1	119.7
O2–C2–N2	109 (3)	123.2	123.6	123.4	123.5	123.7	122.9
N3–C2–N2	126 (2)	119.1	118.3	118.2	118.0	118.2	117.4
O1–C1–N1	127 (3)	123.2	123.6	123.4	123.5	123.7	122.9
N1–C1–N3	118 (3)	119.1	118.3	118.2	118.0	118.2	117.4
O1–C1–N3	116 (3)	117.7	118.0	118.4	118.5	118.1	119.7
Br1–Au–N1	89.6 (5)	88.9	89.1	89.0	89.2	88.9	
Br1–Au–Br2	91.9 (1)	93.0	93.1	95.0	94.5	93.2	
Br2–Au–N2	85.5 (6)	89.0	89.1	89.0	89.2	88.9	
N1–Au–N2	93.1 (8)	89.1	88.7	87.1	87.0	89.0	

coordination plane are 176.7 and 177.4°, respectively. The six-membered chelate Au–N1–C1–N3–C2–N2 ring is almost planar with maximum atomic deviation from the least-squares plane of 0.16 Å. The geometry of the complex anion $[\text{Au}(\text{Biu})\text{Br}_2]^-$ is approximately planar with small deviation (0.31 Å) in the coordination plane of atoms O2 and Br2.

No Au(III)–Au(III) interaction is observed in the crystal as the closest distance of two neighboring Au ions is 6.9 Å (i.e. the unit-cell repeat in the *c* direction) due most likely to the presence of bulky counter ion Ph_4P^+ .

Ab initio calculations on both complexes and biuret at different computational levels were carried out. The structural parameters of these compounds are listed in Table II. In general, comparing computational and X-ray data for $[\text{Au}(\text{Biu})\text{Br}_2]^-$, best results were obtained at the ECP-31G(d) level. For that reason the calculations for $[\text{Au}(\text{Biu})\text{Cl}_2]^-$ and biuret were performed at the same level.

An IR study of the ligand and its complexes was made in order to compare the structures of the complexes. Selected IR data (calculated and experimental) are shown in Tables III and IV, respectively. It is evident that the experimental and calculated data for both complexes are very similar. In the IR spectra the most significant changes are observed in the regions of stretching (3400–3100 cm^{-1}) and bending NH vibrations (1280–1270 cm^{-1}) as expected for coordination via the terminal deprotonated amino groups [24–26]. The bands due to the stretching asymmetric, symmetric and bending NH_2 vibrations of the free ligand are lacking. Instead, in the spectra of the Complexes **1** and **2**, other bands occur at 3378, 3233 cm^{-1} and 3378,

TABLE III Selected *ab initio* calculated at HF/ECP-31G(d) level and experimental IR data for biuret. Frequencies are in cm^{-1} and intensities (in brackets) are in km/mol

Calculated	Experimental	Assignment
3437 (0), 3437 (141), 3339 (46), 3338 (53)	3411 s, 3250–3200	NH ₂ str.
3399 (98)	3403 s	NH str.
1762 (500), 1756 (871)	1724 s, 1682 s	C=O str.
1578 (86)	1616 sh	NH ₂ bend.
1563 (275), 1385 (306), 1312 (362)	1584 m, 1350 sh, 1328 m	HNC bend. +CN str.
1404 (84)	1422 m	CN str.
1126 (5)	1132 w	NH ₂ rock.
1096 (131), 985 (13)	1079 w, 947 v.w.	CN str. +ring def. i.p.

TABLE IV Selected *ab initio* calculated at HF/ECP-31G(d) level and experimental IR data for [Au(Biu)Br₂]⁻ and [Au(Biu)Cl₂]⁻. Frequencies are in cm^{-1} and intensities (in brackets) are in km/mol

[Au(Biu)Br ₂] ⁻			[Au(Biu)Cl ₂] ⁻		
Calculated	Exptl	Assignment	Calculated	Exptl	Assignment
3425 (35)	3434 w	N1–H1 str.	3426 (41)	3450 w	N1–H1 str.
3410 (89)	3378 m	N3–H3 str.	3411 (86)	3378 w	N3–H3 str.
3384 (37)	3233 m	N2–H2 str.	3385 (44)	3239 m	N2–H2 str.
1677 (923)	1649 s	H3–N3–C1 bend. + C2–O2 + C1–O1	1679 (922)	1651 s	H3–N3–C1 bend. + C2–O2 + C1–O1
1661 (1207)	1620 s	C1–O1 + C2–O2 + ring def.	1664 (1126)	1623 s	C1–O1 + C2–O2 + ring def.
1432 (834)	1468 m	N1–C1 + C2–N2 + C1–N3 + N3–C2	1434 (725)	1439 m	N1–C1 + C2–N2 + C1–N3 + N3–C2
1294 (36)	1300 m	H2–N2–C2 bend. + H1–N1–C1	1295 (26)	1305 m	H2–N2–C2 bend. + H1–N1–C2
1277 (137)	1272 m	ring def. in plane	1280 (149)	1277 m	ring def. in plane
1036 (71)	1066 w	ring def. in plane	1037 (67)	1068 w	ring def. in plane
929 (29)	823 w	ring def. + C1–N3 + N3–C2 + C1–N3–C2	931 (21)	818 w	ring def. + C1–N3 + N3–C2 + C1–N3–C2
748 (87)		ring def. out of plane	751 (32)		Au–N str.
745 (32)		Au–N str. + Au–N–C bend.	749 (86)		ring def. out of plane
619 (235)	575 w	H1–N1–C1–N3 tors.	553 (253)	580 w	H1–N1–C1–N3 tors.
200 (18)	219 w	Au–Br str.	311 (87)	349 w	Au–Cl str.
194 (14)	206 w	Au–Br str.	297 (33)	329 w	Au–Cl str.

3239 cm^{-1} , respectively, are assigned to the middle and terminal NH groups. It should be also noted that the very intense bands at 1724 and 1682 cm^{-1} observed in the biuret spectrum and assigned to $\nu_{\text{C=O}}$ are also shifted to lower frequencies (Table IV). These bands are strongly affected because they are mixed carbonyl stretching and HNC bending vibrations. On the other side coordination evidently causes strong delocalization of the electron density in the framework of the planar chelate ring. This is consistent with calculated bond lengths for both complexes and biuret. In the complexes the C=O and N3–C bonds become shorter and N2–C2 and N1–C1 bonds longer.

According to the calculated data the Au–N stretching band should be observed in the 745–751 cm^{-1} range (Table IV). In this region, however, intense absorbance due to the counter ions is present not allowing identification of this band. Bands due to Au–Br and Au–Cl are found in the range 220–200 and 350–330 cm^{-1} , respectively as expected from literature data [27,28].

The similarities between the ¹H NMR data for both complexes prove unambiguously the presence of the bulky counter ion and provide evidence for coordination via the terminal NH groups. The corresponding peaks for terminal and middle NH protons in the free ligand are observed at 0.39 and 1.54 ppm, respectively. Coordination causes significant downfield shifts of both the terminal and middle NH peaks. In the spectrum of **2** no peak due to the middle NH is observed due most likely to its low intensity.

On the basis of all these data it might be concluded that doubly-deprotonated biuret ion is suitable for stabilization of Au(III) forming planar *cis*-Au(Biu)X₂ complexes ion of similar structure.

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Supplementary Materials

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 165610. This information can be obtained from the CCDC Home Page on the Worldwide Web (<http://www.ccdc.cam.ac.uk>) or by E-mail: deposit@ccdc.cam.ac.uk

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