Crystal structure of bis(3,3'-trimethylene-2,2'-biquinolinium)(1+) dibromoaurate(I)(1-) tetrabromoaurate(III)(1-), (C₂₁H₁₆N₂H)₂[AuBr₂][AuBr₄], a mixed valence Au(I)/Au(III) salt

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Received December 17, 1999, CCDC-No. 1267/371

Abstract

C₂₁H₁₇AuBr₃N₂, triclinic, *P* $\bar{1}$ (No. 2), *a* = 10.296(2) Å, *b* = 12.875(3) Å, *c* = 8.901(2) Å, α = 105.84(2)°, β = 109.52(1)°, γ = 74.66(2)°, *V* = 1050.1 Å³, *Z* = 2, $\bar{\kappa}_{\text{gt}}(\bar{F})$ = 0.046, *wR*(*F*) = 0.042, *T* = 293 K.

Source of material

A suspension of 3,3'-trimethylene-2,2'-biquinoline (0.5 mmol in absolute methanol) was dropped into a methanolic solution of KAuBr₄ (0.5 mmol). The brownish red suspension was refluxed under nitrogen (1 h). KBr was removed by filtration and the resulting solution was evaporated to dryness under reduced pressure. Recrystallization from dichloromethane provided dark red crystals [1].

Discussion

Instead of the expected fivefold coordinated gold(III) the crystal contains linear dibromoaurate(I)(1-) anions (*d*(Au—Br) = 237.0 pm) as well as square planar tetrabromoaurate(III)(1-) anions (*d*(Au—Br) = 242.9 pm). The two 3,3'-trimethylene-2,2'-biquinolinium(1+) cations (C₂₁H₁₆NH)⁺ both are connected with the [AuBr₄]¹⁻ anion by two bifurcated (three-center) Br...H(N)...Br hydrogen bonds (*trans* configuration, *d*(Br...H) = 297 pm). Only this H atom allows a stable refinement. The partial reduction to Au(I) is not explainable yet. The protonation of the chelate ligand indicates the presence of the free H[AuBr₄] acid in the course of the reaction. The linear [AuBr₂]¹⁻ anions are located in large cavities without further coordinating N-contacts and they are aligned toward the planes of two pyridinium fragments of adjacent chelate ligands. These details rule out that the linear [AuBr₂] unit may be a dibromoauronium(III)(1+) cation as in [AuBr₂py] (*d*(Au—Br) = 242.3 pm) [2]. For the corresponding [AuCl₄]¹⁻ anions, see [3].

Table 1. Data collection and handling.

Crystal:	dark red prism, size 0.25 × 0.4 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	127.20 cm ⁻¹
Diffractometer, scan mode:	Siemens R3m/V, Wyckoff
2 θ_{max} :	55°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	4526, 4526
Criterion for <i>F</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>F</i> _{obs} > 3 σ (<i>F</i> _{obs}), 3825
<i>N</i> (<i>param</i>) _{refined} :	249
Program:	SHELXTL-plus [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	2i	0.10687	−0.18044	0.60709	0.08(4)
H(3A)	2i	−0.076(1)	−0.2837(9)	0.542(1)	0.08
H(4A)	2i	−0.171(1)	−0.437(1)	0.385(1)	0.08
H(5A)	2i	−0.074(1)	−0.557(1)	0.185(1)	0.08
H(6A)	2i	0.127(1)	−0.532(1)	0.149(1)	0.08
H(8A)	2i	0.303(1)	−0.4080(9)	0.213(1)	0.08
H(10A)	2i	0.442(1)	−0.281(1)	0.245(1)	0.08
H(10B)	2i	0.395(1)	−0.161(1)	0.333(1)	0.08
H(11A)	2i	0.622(1)	−0.195(1)	0.457(1)	0.08

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(11B)	2i	0.622(1)	−0.316(1)	0.458(1)	0.08
H(12A)	2i	0.546(1)	−0.266(1)	0.677(1)	0.08
H(12B)	2i	0.656(1)	−0.191(1)	0.717(1)	0.08
H(14A)	2i	0.589(1)	−0.001(1)	0.820(1)	0.08

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16A)	2i	0.513(1)	0.195(1)	0.964(1)	0.08
H(17A)	2i	0.333(1)	0.331(1)	1.038(1)	0.08
H(18A)	2i	0.100(1)	0.302(1)	0.953(1)	0.08
H(19A)	2i	0.045(1)	0.1362(9)	0.783(1)	0.08

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Au(1)	1a	1.0	0.0	1.0	0.0366(3)	0.0456(4)	0.0376(3)	−0.0096(3)	0.0147(2)	0.0017(2)
Au(2)	1e	1/2	1/2	0	0.0456(3)	0.0434(4)	0.0647(4)	−0.0133(3)	0.0202(3)	−0.0017(3)
Br(1)	2i	0.8605(1)	−0.0377(1)	0.7183(1)	0.0475(6)	0.0656(8)	0.0426(5)	−0.0110(6)	0.0087(5)	−0.0016(5)
Br(2)	2i	1.1531(1)	−0.1776(1)	0.9511(1)	0.0596(7)	0.0563(8)	0.0523(6)	0.0027(6)	0.0189(5)	0.0021(5)
Br(3)	2i	0.3930(1)	−0.4248(1)	−0.2376(2)	0.0695(8)	0.0635(9)	0.0790(8)	−0.0257(7)	0.0048(7)	0.0153(7)
N(1)	2i	0.1473(8)	−0.2280(7)	0.5300(9)	0.040(4)	0.036(5)	0.040(4)	−0.014(4)	0.019(3)	−0.005(3)
C(2)	2i	0.088(1)	−0.3185(8)	0.439(1)	0.046(5)	0.031(5)	0.041(5)	−0.015(4)	0.009(4)	−0.002(4)
C(3)	2i	−0.034(1)	−0.3345(9)	0.462(1)	0.054(6)	0.040(6)	0.058(6)	−0.014(5)	0.025(5)	−0.004(5)
C(4)	2i	−0.089(1)	−0.424(1)	0.370(1)	0.057(7)	0.060(8)	0.066(7)	−0.030(6)	0.022(6)	−0.008(6)
C(5)	2i	−0.032(1)	−0.496(1)	0.251(1)	0.063(7)	0.051(7)	0.067(7)	−0.031(6)	0.022(6)	−0.013(6)
C(6)	2i	0.085(1)	−0.480(1)	0.228(1)	0.076(8)	0.049(7)	0.049(6)	−0.018(6)	0.018(6)	−0.016(5)
C(7)	2i	0.145(1)	−0.3850(9)	0.321(1)	0.050(6)	0.039(6)	0.043(5)	−0.010(5)	0.009(4)	0.000(4)
C(8)	2i	0.263(1)	−0.3601(9)	0.296(1)	0.052(6)	0.052(7)	0.046(5)	−0.009(5)	0.023(5)	−0.006(5)
C(9)	2i	0.320(1)	−0.2715(9)	0.386(1)	0.042(5)	0.043(6)	0.043(5)	−0.008(5)	0.018(4)	0.002(4)
C(10)	2i	0.429(1)	−0.236(1)	0.346(1)	0.047(6)	0.062(8)	0.047(5)	−0.006(5)	0.029(5)	0.000(5)
C(11)	2i	0.572(1)	−0.242(1)	0.474(1)	0.054(7)	0.09(1)	0.061(7)	−0.019(7)	0.030(6)	0.004(7)
C(12)	2i	0.566(1)	−0.206(1)	0.649(1)	0.042(6)	0.061(8)	0.054(6)	−0.009(5)	0.014(5)	0.008(5)
C(13)	2i	0.456(1)	−0.1040(9)	0.682(1)	0.041(5)	0.043(6)	0.038(5)	−0.008(5)	0.019(4)	0.001(4)
C(14)	2i	0.492(1)	−0.008(1)	0.780(1)	0.038(5)	0.066(8)	0.043(5)	−0.023(5)	0.013(4)	0.006(5)
C(15)	2i	0.386(1)	0.0840(9)	0.826(1)	0.046(5)	0.044(6)	0.037(5)	−0.021(5)	0.011(4)	0.003(4)
C(16)	2i	0.418(1)	0.183(1)	0.926(1)	0.056(7)	0.063(8)	0.044(5)	−0.027(6)	0.010(5)	0.003(5)
C(17)	2i	0.312(1)	0.262(1)	0.971(1)	0.071(8)	0.049(7)	0.051(6)	−0.032(6)	0.014(6)	0.000(5)
C(18)	2i	0.172(1)	0.246(1)	0.919(1)	0.063(7)	0.047(7)	0.057(6)	−0.014(6)	0.019(5)	−0.002(5)
C(19)	2i	0.140(1)	0.1480(9)	0.819(1)	0.048(6)	0.039(6)	0.052(6)	−0.012(5)	0.017(5)	0.001(5)
C(20)	2i	0.246(1)	0.0661(9)	0.770(1)	0.045(5)	0.041(6)	0.033(4)	−0.013(4)	0.012(4)	0.004(4)
N(21)	2i	0.2102(8)	−0.0299(7)	0.6683(9)	0.041(4)	0.041(5)	0.039(4)	−0.015(4)	0.015(3)	0.003(3)
C(22)	2i	0.312(1)	−0.1081(8)	0.624(1)	0.040(5)	0.039(6)	0.038(5)	−0.011(4)	0.012(4)	0.005(4)
C(23)	2i	0.2605(9)	−0.2063(9)	0.511(1)	0.038(5)	0.041(5)	0.037(5)	−0.010(4)	0.014(4)	−0.000(4)

References

- Schmidt, R.; Binder, H.: Z. Anorg. Allg. Chem., in preparation.
- Peters, K.; Peters, E.-M.; von Schnering, H. G.; Hönle, W.; Schmidt, R.; Binder, H.: Crystal structure of pyridino gold(III) bromide, [AuBr₂(py)₂]⁺[AuBr₄][−][AuBr₃py]₂, a frozen-in autoionization system. Z. Kristallogr. NCS 215 (2000) 411–412.
- Adams, H.-N.; Strähle, J.: Darstellung und Struktur von [Hpy][AuCl₄], AuCl₃py, [AuCl₂(py)₂]Cl · H₂O und [AuCl₂(py)₂][AuCl₂]. Z. Anorg. Allg. Chem. 485 (1982) 65–80.
- Sheldrick, G. M.: Program Package SHELXTL-Plus. Release 4.1, Siemens Analytical X-Ray Instruments Inc., Madison (WI 53719), USA 1990.