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Synthesis, Structure, and Properties of Trichloro- and Tribromo(2-(2′-pyridyl)quinoline)gold(III)

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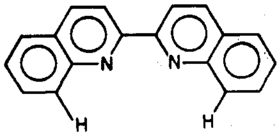
The title complexes Au(pq)Cl_3 and Au(pq)Br_3 (pq = 2-(2′-pyridyl)quinoline) have been synthesized and their crystal and molecular structures determined from X-ray data obtained by counter methods. The compounds are isomorphous and crystallize in the space group $P2_12_12_1$, with $Z = 4$ in unit cells of dimensions $a = 7.711$ (7), $b = 10.04$ (1), and $c = 19.34$ (4) Å (Au(pq)Cl_3) and $a = 8.050$ (4), $b = 10.13$ (2), and $c = 19.52$ (1) Å (Au(pq)Br_3). The structures were solved by the heavy-atom method and refined by full-matrix least squares to $R = 6.5\%$ (Au(pq)Cl_3, 1511 reflections) and $R = 5.1\%$ (Au(pq)Br_3, 907 reflections). The compounds consist of discrete diamagnetic five-coordinated molecules. The distribution of the ligands about the metal is approximately square pyramidal with the axial ligand displaced from the vertical and at a relatively great distance from the metal, so that they may also be described as strongly distorted square planar. The direction of the distortion is such as to reduce the energy of the high-spin (triplet) state but not enough to produce a high-spin ground state.

Introduction

Gold compounds have been of long-standing biological interest for use as drugs and catalysts in biological systems.[1] The observation of five-coordinated complexes is important in the understanding of gold(III) chemistry. Many reactions of gold(III) are proposed to proceed via a five-coordinated intermediate. The slow kinetics[2] of ligand exchange and substitution with gold(III) compounds may be explained by the relative instability of the five-coordinated intermediates compared with the square-planar compounds. Five-coordinated intermediates are also important in the action of gold(III) on certain amino acids. Gold(III) has been shown to stereospecifically drive the oxidation of (*S*)-methionine to (*S*)-methionine *S*-sulfoxide,[3] a reaction which presumably proceeds via a five-coordinate intermediate with the amino acid chelated to the gold(III). The oxidative attack is then confined to an approach that is sterically limited by the other ligands (chlorine) on the gold.

Ring-substituted dipyridyl, phenanthroline, and terpyridyl ligands induce a variety of unusual structures with transition metals, including pseudotetrahedral, five-coordinated monomeric, or dimeric compounds of manganese(II), nickel(II), and copper(II).[4-8] Stable five-coordinated gold complexes have been obtained with two such ligands,[9,10] (I) 2,2′-biquinolyl and (II) 2,9-dimethylphenanthroline, due to extreme ligand–ligand steric crowding caused by the ring substituents. An examination of these structures leads us to postulate that five-coordinated complexes could be formed with the much less sterically hindered ligand (III) 2-(2′-pyridyl)quinoline. We report here on the synthesis and crystal structures of the five-coordinated gold(III) complexes trichloro- and tribromo(2-(2′-pyridyl)quinoline)gold(III), Au(pq)X_3, X = Cl, Br.



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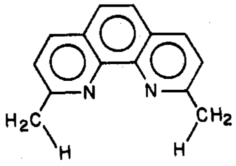

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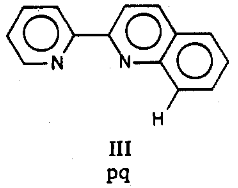
dmp



III
pq

Experimental Section

Preparation of Compounds. Au(pq)Cl_3. Sodium tetrachloroaurate(III) in absolute ethanol was added to a stoichiometric amount of pq in benzene. The orange-yellow crystals precipitated slowly and were filtered, washed with benzene and ethanol, and dried. Crystals suitable for X-ray study were obtained by slow evaporation of a saturated solution of the compound in nitrobenzene.

Au(pq)Br_3. The preparation of the compound is as above using $NaAuBr_4$. The product is formed as orange-red crystals. Sodium tetrabromoaurate(III) was prepared by repeatedly dissolving $NaAuCl_4$ in concentrated HBr and then heating to dryness.

2-(2′-Pyridyl)quinoline. This ligand was prepared by the method of Smirnoff.[11] *o*-Aminobenzaldehyde, freshly prepared by steam distillation,[12] in ethanol is mixed with a stoichiometric amount of 2-acetylpyridine. After a stoichiometric amount of NaOH was added as 1 N NaOH, the mixture was refluxed for 1 h on a steam bath. The mixture was decolorized with charcoal, filtered, and diluted with hot water until turbid. The compound crystallized on cooling in ice, was filtered, and recrystallized twice from methanol.

Magnetic Susceptibility. Measurements were made on a superconducting susceptometer and the complexes were found to be diamagnetic.

Crystal Data for Au(pq)Cl_3. $AuCl_3N_2C_{14}H_{10}$: mol wt 510; space group $P2_12_12_1$; $Z = 4$; $a = 7.711$ (7), $b = 10.04$ (1), $c = 19.34$ (4) Å; $V = 1498$ Å^3; $\rho_{calcd} = 2.13$ g cm^{-3}, $\rho_{obsd} = 2.2$ g cm^{-3}; μ(Mo Kα) = 100 cm^{-1}; crystal dimensions (mm from centroid) (100) 0.32, ($\bar{1}00$) 0.32, (010) 0.40, ($0\bar{1}0$) 0.40, (001) 0.038, ($00\bar{1}$) 0.038, (110) 0.30, ($\bar{1}\bar{1}0$) 0.30, ($1\bar{1}0$) 0.295, ($\bar{1}10$) 0.295; maximum and minimum transmission coefficients 0.58 and 0.26.

Crystal Data for Au(pq)Br_3. $AuBr_3N_2C_{14}H_{10}$, mol wt 643; space group $P2_12_12_1$; $Z = 4$; $a = 8.050$ (4), $b = 10.13$ (2), $c = 19.52$ (1) Å; $V = 1592$ Å^3; $\rho_{calcd} = 2.68$ g cm^{-3}, $\rho_{obsd} = 2.7$ g cm^{-3}; μ(Mo Kα) = 175 cm^{-1}, crystal dimensions ($2\bar{1}0$) 0.07, ($\bar{2}10$) 0.07, (011) 0.05, ($0\bar{1}\bar{1}$) 0.05, ($01\bar{1}$) 0.05, ($0\bar{1}1$) 0.05; maximum and minimum transmission coefficients 0.32 and 0.18.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an ori-

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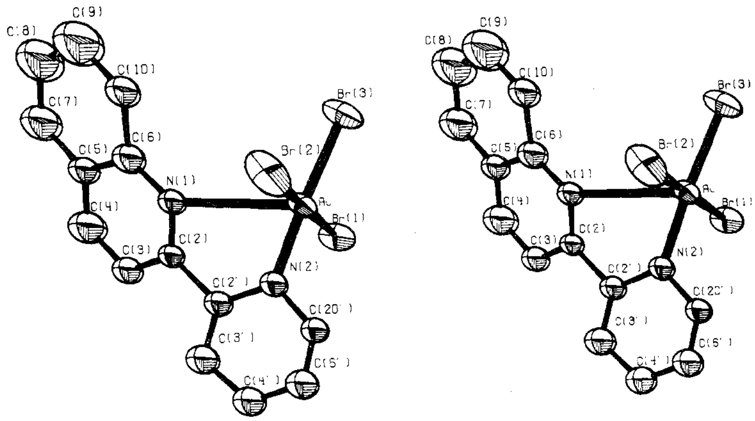

Figure 1. Stereoview of Au(pq)Br_3.

entation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory, but the Au(pq)Br_3 crystal was by far the better one.

Collection and Reduction of Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $0 < 2\theta < 50°$ for Au(pq)Cl_3 and $0 < 2\theta < 48°$ for Au(pq)Br_3. Scan widths (SW) were calculated from the formula SW = $A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.30° for Au(pq)Br_3 and 0.90 and 0.35° for Au(pq)Cl_3. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. The validity of the absorption correction was confirmed by rotating about the diffraction vector ("ψ scans") for several strong reflections; this showed that the transmission coefficients varied as expected with path length for each crystal. After averaging the intensities of equivalent reflections, the data reduced to 1779 independent intensities for Au(pq)Cl_3 and 1505 for Au(pq)Br_3, of which 1511 and 907 for the two complexes respectively had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[13] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structures. The positions of the gold atom and three bromine atoms in Au(pq)Br_3 were obtained from a three-dimensional Patterson function calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen and some hydrogen atoms.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[14] and those for hydrogen from Stewart et al.[15] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using the values of Cromer and Ibers[16] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Refinement on Au(pq)$Cl_3$ was carried out using the parameters for Au(pq)Br_3 as starting values. Four reflections were found to be suffering from secondary extinction effects and were eliminated from the data set of Au(pq)Cl_3.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the remaining hydrogen atoms, which were included in the refinement with fixed temperature factors (5.0 Å^2).

The high-energy radiation used predetermines that the right and wrong choices for the absolute configuration will not greatly affect the refinement of the two complexes and therefore that the choice cannot safely be made on the intensities of a few reflections. For each complex, both configurations were refined to completion on all intensity data. The absolute configuration was chosen on the basis of slightly better agreement based on R_w and the choice was confirmed by a detailed comparison of observed and calculated intensities of both weak and strong reflections.

The models converged with $R = 6.5$, $R_w = 7.5\%$ for Au(pq)Cl_3 and $R = 5.1$, $R_w = 5.4\%$ for Au(pq)Br_3. A structure factor calculation with all observed and unobserved reflections included (no refinement) give $R = 7.3$ and 6.7% for the two complexes, respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[17] The principal programs used are as previously described.[18]

Results and Discussion

Stable, neutral complexes of pq are formed with gold(III) halides. However, the precipitation of the compounds Au(pq)Cl_3 and Au(pq)Br_3 takes place over several hours, even though the compounds are insoluble in the reaction mixtures. This contrasts with the very rapid precipitation of other transition metal complexes with pq in similar reactions. The slow reaction is due to the relative instability of the five-coordinated complex relative to the square-planar starting material, being forced to completion only by the removal of the insoluble product. This would relate directly to the slow process of ligand exchange and substitution reactions observed with gold(III) compounds.[3]

Final positional and thermal parameters for Au(pq)Cl_3 and Au(pq)Br_3 are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. The light atom values for bond lengths, etc., have relatively high standard deviations due to the large scattering power accounted for by the heavy atoms. Because of the close structural similarity between the two complexes, only Au(pq)Br_3 is shown in the diagrams. Figure 1 is a stereopair view of Au(pq)Br_3 and Figure 2 shows the molecular packing in the unit cell.

The ligand environment of the gold atom is distorted square pyramidal in each case, with the gold atom raised above the base of the square pyramid by 0.04 Å in Au(pq)Cl_3 and 0.08 Å in Au(pq)Br_3. The main distortion from square-pyramidal geometry in each structure is the elongated Au–N(1) bond (2.66 (2) Å in Au(pq)Br_3 and 2.68 (1) Å in Au(pq)Cl_3), and the tilt of the axis of the pyramid from the vertical, as defined

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

A. Au(pq)Cl_3

atom	*x*	*y*	*z*	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Au	0.2995 (1)	0.4290 (1)	0.66939 (6)	2.65 (3)	1.26 (3)	3.73 (4)	0.04 (4)	0.03 (5)	−0.47 (4)
Cl(1)	0.587 (1)	0.4316 (9)	0.6463 (5)	2.9 (3)	2.4 (3)	7.6 (5)	−0.3 (3)	0.3 (3)	−0.9 (4)
Cl(2)	0.014 (1)	0.4163 (12)	0.6976 (6)	2.4 (3)	6.0 (5)	6.9 (5)	−0.4 (4)	0.1 (3)	−1.7 (5)
Cl(3)	0.314 (1)	0.6408 (8)	0.7110 (6)	5.8 (4)	1.4 (3)	7.8 (5)	0.4 (3)	0.4 (5)	−2.0 (3)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(1)	0.233 (3)	0.415 (3)	0.534 (1)	3.1 (5)	C(4′)	0.304 (5)	−0.032 (4)	0.599 (2)	4.4 (7)
N(2)	0.292 (4)	0.231 (3)	0.632 (1)	3.5 (5)	C(5′)	0.298 (5)	0.006 (5)	0.666 (2)	5.0 (8)
C(2)	0.305 (4)	0.311 (3)	0.517 (1)	2.6 (5)	C(6′)	0.296 (4)	0.137 (3)	0.686 (1)	2.8 (5)
C(3)	0.367 (4)	0.286 (3)	0.451 (2)	2.8 (5)	H(3)	0.4045	0.1960	0.4435	3.5
C(4)	0.362 (5)	0.383 (4)	0.403 (2)	4.6 (8)	H(4)	0.4041	0.3684	0.3558	3.5
C(5)	0.298 (5)	0.498 (4)	0.421 (2)	4.2 (7)	H(7)	0.3302	0.6097	0.3228	3.5
C(6)	0.226 (3)	0.518 (3)	0.488 (1)	2.1 (5)	H(8)	0.2043	0.8198	0.3664	3.5
C(7)	0.291 (5)	0.622 (4)	0.374 (2)	4.7 (8)	H(9)	0.0936	0.8357	0.4748	3.5
C(8)	0.211 (6)	0.737 (4)	0.397 (2)	5.3 (9)	H(10)	0.0969	0.6493	0.5588	3.5
C(9)	0.152 (5)	0.749 (5)	0.461 (2)	5.0 (9)	H(3′)	0.3097	0.0287	0.5009	3.5
C(10)	0.156 (3)	0.644 (3)	0.506 (1)	2.0 (5)	H(4′)	0.3111	−0.1176	0.5912	3.5
C(2′)	0.297 (4)	0.197 (3)	0.569 (1)	2.1 (4)	H(5′)	0.2843	−0.0739	0.7048	3.5
C(3′)	0.303 (4)	0.063 (3)	0.551 (2)	3.5 (6)	H(6′)	0.3417	0.1678	0.7413	3.5

B. Au(pq)Br_3

atom	*x*	*y*	*z*	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Au	0.2999 (2)	0.4219 (1)	0.67095 (7)	1.81 (4)	2.44 (4)	2.74 (4)	0.01 (7)	0.08 (6)	−0.65 (8)
Br(1)	0.5961 (4)	0.4190 (5)	0.6484 (2)	2.1 (1)	3.5 (2)	5.5 (2)	−0.3 (2)	0.3 (1)	−0.3 (2)
Br(2)	0.0074 (4)	0.4106 (6)	0.7001 (2)	1.8 (1)	7.8 (3)	5.7 (2)	−0.3 (2)	0.7 (2)	−2.9 (3)
Br(3)	0.3160 (6)	0.6376 (4)	0.7184 (2)	4.9 (2)	3.1 (2)	5.8 (2)	−0.0 (2)	0.4 (2)	−1.7 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(1)	0.243 (3)	0.420 (3)	0.538 (1)	2.1 (5)	C(4′)	0.311 (5)	−0.030 (4)	0.599 (2)	3.3 (8)
N(2)	0.297 (4)	0.238 (3)	0.636 (1)	2.3 (5)	C(6′)	0.299 (5)	0.004 (3)	0.663 (2)	3.4 (7)
C(2)	0.306 (4)	0.312 (3)	0.518 (2)	1.9 (6)	C(20′)	0.297 (4)	0.130 (3)	0.680 (2)	2.4 (6)
C(3)	0.363 (4)	0.293 (4)	0.453 (2)	2.6 (8)	H(3)	0.38 (3)	0.20 (3)	0.43 (1)	2.7
C(4)	0.361 (5)	0.396 (4)	0.409 (2)	4.0 (10)	H(4)	0.34 (3)	0.40 (2)	0.38 (1)	1.6
C(5)	0.295 (4)	0.510 (3)	0.427 (2)	2.5 (7)	H(7)	0.30 (3)	0.59 (3)	0.34 (1)	1.5
C(6)	0.238 (4)	0.518 (4)	0.493 (2)	2.9 (8)	H(8)	0.21 (3)	0.77 (3)	0.39 (1)	2.6
C(7)	0.290 (5)	0.620 (4)	0.383 (2)	4.3 (9)	H(9)	0.09 (3)	0.79 (3)	0.49 (1)	2.7
C(8)	0.215 (6)	0.735 (5)	0.406 (2)	5.6 (11)	H(10)	0.15 (4)	0.65 (3)	0.56 (2)	5.9
C(9)	0.140 (6)	0.742 (5)	0.471 (2)	6.1 (13)	H(3′)	0.34 (4)	0.08 (3)	0.49 (1)	5.8
C(10)	0.154 (4)	0.641 (4)	0.513 (2)	3.0 (8)	H(4′)	0.31 (4)	−0.12 (3)	0.59 (1)	4.8
C(2′)	0.306 (4)	0.199 (3)	0.569 (2)	2.3 (7)	H(5′)	0.29 (3)	−0.06 (2)	0.70 (1)	2.6
C(3′)	0.312 (5)	0.071 (4)	0.548 (2)	3.3 (7)	H(6′)	0.30 (3)	0.16 (2)	0.71 (1)	2.6

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Bond Lengths (Å) for Au(pq)Cl_3 and Au(pq)Br_3

	X = Cl	X = Br		X = Cl	X = Br
Au-X(1)	2.261 (4)	2.422 (3)	C(4)-C(5)	1.30 (2)	1.32 (4)
Au-X(2)	2.271 (4)	2.423 (4)	C(5)-C(6)	1.43 (2)	1.38 (4)
Au-X(3)	2.277 (4)	2.385 (3)	C(5)-C(7)	1.54 (2)	1.41 (4)
Au-N(1)	2.68 (2)	2.64 (2)	C(6)-C(10)	1.42 (2)	1.47 (4)
Au-N(2)	2.11 (2)	1.99 (2)	C(7)-C(8)	1.38 (2)	1.38 (4)
N(1)-C(2)	1.22 (2)	1.27 (3)	C(8)-C(9)	1.33 (2)	1.42 (4)
N(1)-C(6)	1.36 (2)	1.32 (3)	C(9)-C(10)	1.37 (2)	1.31 (4)
N(2)-C(2′)	1.26 (1)	1.36 (3)	C(2′)-C(3′)	1.39 (2)	1.37 (4)
N(2)-C(6′)	1.42 (2)	1.40 (3)	C(3′)-C(4′)	1.34 (2)	1.44 (4)
C(2)-C(3)	1.40 (2)	1.37 (3)	C(4′)-C(5′)	1.34 (2)	1.31 (4)
C(2)-C(2′)	1.52 (2)	1.52 (3)	C(5′)-C(6′)	1.38 (2)	1.32 (3)
C(3)-C(4)	1.34 (2)	1.35 (4)			

by the angle N(1)–Au–N(2) (70.2 (9)° in Au(pq)Br_3 and 68.0 (4)° in Au(pq)Cl_3). The axial Au–N bond, which averages 2.67 Å in the two very similar complexes, is fairly weak (covalent Au–N = 1.40 + 0.74 = 2.04 Å) but still much shorter than the van der Waals contact distance (nonbonded Au–N = 2.2 + 1.5 = 3.7 Å).[19] Axial distortion of the normal planar gold(III) geometry toward square pyramidal lowers the energy of the lowest lying triplet state with respect to the singlet ground state. Such distortion observed in the five-coordinated complexes Au(biq)Cl_3, Au(dmp)Cl_3, and Au(dmp)Br_3 was insufficient to affect the magnetic properties; the compounds were observed to be diamagnetic.[10] The axial distortion is even weaker in the present complexes Au(pq)Br_3 and Au(pq)Cl_3, so that a singlet ground state would be predicted, and is confirmed by the observed diamagnetism of the compounds. In each of the known five-coordinated gold(III) complexes (Table IV), the elongation of the axial bond and its angular displacement from the vertical (*z*) axis minimizes the interaction with the d_{z^2} orbital. Thus the stereochemistry adopted is such as to minimize the possibility of high-spin ground states.

Steric constraints prevent more than one halogen sharing the plane of the very sterically hindered bidentate ligands biq (I) and dmp (III). Thus, the preferred planar geometry of gold(III) can most nearly be achieved by bonding to one of the nitrogen atoms of I and II. The approximate coplanarity of the three halogen atoms and one of the ligand nitrogens automatically brings the other ligand nitrogen to within bonding distance of the metal atom. The metal–ligand bond to this axial nitrogen atom will be weakened by the relative instability of five-coordinated gold(III) and strong steric interaction of substituent protons adjacent to this nitrogen and the nearest coordinated halogen atom.[10] In pq, the steric constraint is less severe, but still results in a five-coordinated complex. The great importance of steric interactions in distorting the various five-coordinated geometries is verified by the fact that the quinoline nitrogen atom forms an elongated axial bond and the pyridine ring is bonded in-plane. However,

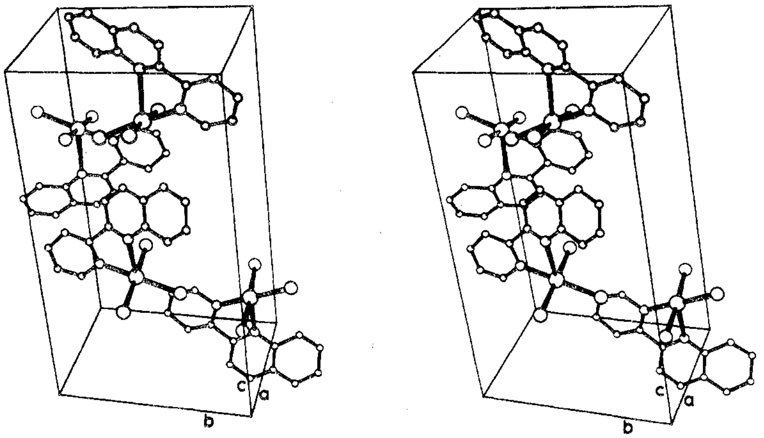

Figure 2. Molecular packing in Au(pq)Br_3.

Table III. Bond Angles (deg) for Au(pq)Cl_3 and Au(pq)Br_3

	X = Cl	X = Br		X = Cl	X = Br
X(1)-Au-X(2)	176.4 (2)	175.4 (2)	C(2)-C(3)-C(4)	120 (1)	119 (3)
X(1)-Au-X(3)	90.7 (1)	91.6 (1)	C(3)-C(4)-C(5)	118 (1)	121 (3)
X(1)-Au-N(1)	89.7 (3)	89.4 (4)	C(4)-C(5)-C(6)	121 (1)	115 (3)
X(1)-Au-N(2)	88.2 (3)	86.3 (7)	C(4)-C(5)-C(7)	126 (1)	123 (3)
X(2)-Au-X(3)	90.8 (2)	90.3 (2)	C(6)-C(5)-C(7)	114 (1)	121 (3)
X(2)-Au-N(1)	92.6 (3)	93.7 (4)	N(1)-C(6)-C(5)	118 (1)	125 (3)
X(2)-Au-N(2)	90.2 (3)	91.5 (7)	N(1)-C(6)-C(10)	122 (1)	119 (3)
X(3)-Au-N(1)	113.9 (3)	113.5 (6)	C(5)-C(6)-C(10)	120 (1)	117 (3)
X(3)-Au-N(2)	178.6 (4)	176.3 (6)	C(5)-C(7)-C(8)	121 (1)	119 (3)
N(1)-Au-N(2)	67.0 (4)	69.6 (8)	C(7)-C(8)-C(9)	122 (2)	121 (4)
Au-N(1)-C(2)	102.2 (7)	103 (2)	C(8)-C(9)-C(10)	121 (2)	119 (3)
Au-N(1)-C(6)	127.2 (8)	130 (2)	C(6)-C(10)-C(9)	123 (1)	123 (3)
C(2)-N(1)-C(6)	119.9 (7)	118 (2)	N(2)-C(2′)-C(3′)	121 (1)	125 (2)
Au-N(2)-C(2′)	125.9 (8)	127 (2)	N(2)-C(2′)-C(2)	116 (1)	124 (3)
Au-N(2)-C(6′)	111.8 (7)	122 (2)	C(3′)-C(2′)-C(2)	116 (1)	121 (2)
C(2′)-N(2)-C(6′)	122 (1)	111 (2)	C(2′)-C(3′)-C(4′)	121 (1)	118 (3)
N(1)-C(2)-C(3)	123 (1)	122 (3)	C(3′)-C(4′)-C(5′)	118 (2)	119 (3)
N(1)-C(2)-C(2′)	117 (1)	117 (2)	C(4′)-C(5′)-C(6′)	123 (2)	120 (4)
C(3)-C(2)-C(2′)	119 (1)	121 (3)	N(2)-C(6′)-C(5′)	115 (1)	127 (3)

Table IV. Comparative Bond Distances of Five-Coordinated Gold(III) Complexes (Å)

	Au-(biq)-Cl_3	Au-(dmp)-Cl_3	Au-(dmp)-Br_3	Au-(pq)-Cl_3	Au-(pq)-Br_3
Au-N (axial)	2.40	2.58	2.61	2.68	2.64
Au-N (plane)	2.28	2.09	2.08	2.11	1.99
Au-Cl (trans)	2.09	2.27	2.40	2.28	2.39
⟨Au-Cl⟩ (cis)	2.37	2.28	2.41	2.27	2.42

the elongation of the axial bond is greater in the Au(pq)X_3 complexes than in Au(biq)Cl_3 or the Au(dmp)X_3 complexes. The most dramatic difference is between Au(pq)X_3 (average 2.67 Å) and Au(biq)Cl_3 (2.40 Å), in which the biq ligand is rotated such as to markedly shorten the axial Au-N bond. This rotation would minimize the interaction of the hydrogen atom adjacent to the *in-plane* nitrogen with the metal d_{z^2} orbital; the absence of a similar hydrogen atom in pq is the most significant difference between the two ligands and is a likely cause of the structural differences between the metal environments in the biq and pq complexes.

The present results show that the unusual five-coordinated gold(III) environment can be sterically forced by the choice of ligands and that this can be achieved with a ligand (pq) which has markedly less severe steric requirements than biq. However, the lesser steric constraint in the pq complex results in a weaker (longer) fifth metal–ligand bond than in the biq complex.

The observation of stable five-coordinate gold(III) complexes is very strong evidence in support of the proposed five-coordinate mechanisms of the chemistry of gold(III) reactions. The only cases of five-coordinated gold(III) occur when a fifth position is sterically forced. This indicates an instability of five-coordinated relative to four-coordinated geometry in the absence of other influences. However, the existence of stable five-coordinated gold(III) complexes provides strong support for such a geometry in a reaction transition state. Thus ligand exchange and substitutions in aqueous and nonaqueous solutions tend to occur stepwise via five-coordinated intermediates but proceed very slowly because of the greater stability of the competing square-planar geometry.[20] On the other hand, it seems unlikely that substitution and exchange reactions proceed via energetically unfavored and never observed three-coordinated intermediates. This is further illustrated by the observation that Me_2AuOH prefers to form a hydroxy-bridged tetramer to achieve square-planar coordination rather than show three-coordination.[21]

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Registry No. Au(pq)Cl_3, 66767-29-1; Au(pq)Br_3, 66767-28-0; $NaAuCl_4$, 15189-51-2; $NaAuBr_4$, 52495-41-7.

Supplementary Material Available: Listings of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Trichloro[1,3-dimethyl-2(3*H*)-imidazolethione]arsenic(III)

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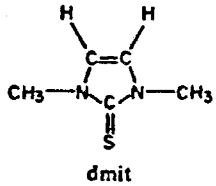
The crystal and molecular structure of $AsCl_3$dmit (dmit = 1,3-dimethyl-2(3*H*)-imidazolethione) has been determined. The compound, $C_3H_8AsCl_3N_2S$, crystallizes in space group $P2_1/c$ with four formula units in a cell of dimensions $a = 8.787$ (2) Å, $b = 10.207$ (1) Å, $c = 12.723$ (3) Å, and $\beta = 108.41$ (3)°. The calculated and observed densities are 1.898 and 1.89 (1) g cm^{-3}, respectively. The structure of $AsCl_3$dmit consists of pseudo-trigonal-bipyramidal molecules (sulfur equatorial) weakly joined into dimeric units of C_i symmetry via axial chlorine bridging. This is in contrast to the known structure of $AsCl_3N(CH_3)_3$ which is best described as a pseudo trigonal bipyramid with the amine bonding in the axial position.

The majority of structural work on adducts of group 5A trihalides has been on complexes with Lewis bases that possess donor sites of relatively high electronegativity and small size such as nitrogen[1,2] and oxygen.[3,4] From the idealized structure[5] for AX_3LE (A = central atom, X = halogen, L = two-electron donor, E = lone pair of electrons), a trigonal-bipyramidal array of substitutents would be predicted assuming a stereoactive lone pair (E). Structures I and II (Figure 1) show the energetically favorable isomeric possibilities for an AX_3LE system.

Both $AsCl_3NMe_3$[6] (Me = methyl) and $SbCl_3NH_2C_6H_5$[2] exhibit structure I due to the relatively high electronegativity and small size of nitrogen.[7] Since all structural studies for AX_3L adducts to date have been concerned with bases of relatively high electronegativity, we were interested in whether a Lewis base with a larger donor site of relatively low electronegativity such as sulfur would give rise to an adduct possessing structure II. The arsenic trichloride adduct of 1,3-dimethyl-2(3*H*)-imidazolethione (dmit) was therefore prepared, and the crystal and molecular structures were determined.



dmit

Experimental Section

The preparation of $AsCl_3$dmit has already been reported.[8] Crystals for X-ray study were grown from a saturated methylene chloride solution at room temperature. A suitable crystal was mounted in a glass capillary, and preliminary precession photography indicated space group $P2_1/c$ from systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The cell dimensions were obtained using Mo Kα_1 radiation (0.709 300 Å) at 25 °C by a least-squares refinement to fit the $\pm 2\theta$ values for 10 high-angle reflections centered on the Picker FACS-1 four-circle diffractometer. The cell parameters are $a = 8.787$ (1) Å, $b = 10.207$ (1) Å, $c = 12.723$ (3) Å, $\beta = 108.41$ (2)°, and $V = 1083$ Å^3. For a formula weight of 309.48 ($C_5H_8AsCl_3N_2S$) and by assuming $Z = 4$, the calculated density is 1.898 g cm^{-3} which agrees well with the observed density of 1.89 g cm^{-3} obtained by flotation in a mixture of *n*-hexane and dibromomethane.

Collection and Reduction of Data. The same crystal used for the unit cell determination was used for data collection. The approximate dimensions were 0.45 mm × 0.65 mm × 0.35 mm with the [$\bar{1}05$] direction coincident with the goniometer rotation axis. Diffractometer data were obtained using Zr-filtered Mo Kα radiation by the θ–2θ scan technique at a takeoff angle of 1.5°. The peaks were scanned at a rate of 1.0°/min from 1.0° on the low-angle side of the Kα_1 peak to 1.0° on the high-angle side of the Kα_2 peak. A scintillation counter was employed to count the diffracted beam, and a Ni foil attenuator was used whenever the count rate exceeded 8000 counts. Stationary-crystal, stationary-counter background counts of 10-s duration were taken at each end of the scan.

A unique data set was collected up to $2\theta = 55°$. The intensities of three reflections were monitored as standards every 100 reflections, and no loss in intensity was observed. Intensities were corrected for background, and standard deviations were assigned according to the equations $I = C - 0.5(t_c/t_b)(B_1 + B_2)$ and $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, where C is the integrated peak count obtained in time t_c and B_1 and B_2 are the background counts obtained in time T_b, all corrected for scalar truncation. A value of 0.05 was used for p. The data were also corrected for Lorentz and polarization effects and subsequently for absorption. A linear absorption coefficient of 41.7 cm^{-1} was calculated to give transmission coefficients ranging from 0.14 to 0.32. Of the 2518 unique reflections collected, 2049 with $I \geq 2\sigma(I)$ were used in the refinement.

Solution and Refinement of Structure. The structure was initially solved by direct methods using a data set collected with Cu Kα radiation and uncorrected for absorption. The details of this data collection and structural solution are reported separately.[9,10] The positions of the nonhydrogen atoms derived from the data set taken with Cu Kα radiation were used as starting positions in refinement of the data set described above. One cycle of isotropic and three cycles of anisotropic least-squares refinement yielded $R_1 = 0.043$ and $R_2 = 0.059$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. In this refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.

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