Zurückziehung

Nach der Veröffentlichung dieser Zuschrift bemerkten die Autoren, dass die kristallographische Strukturbestimmung von $[NEt_4][HgCl_2][HgCl_3]$ bereits beschrieben wurde (*Acta Cryst. E* **2002**, *58*, m534). Zellparameter und Strukturdaten stimmen mit den Werten überein, die die Autoren erhielten und einer Verbindung der Zusammensetzung $[NEt_4][AuCl_2][AuCl_3]$ zuschrieben. Zweifellos wurde hier die Quecksilberverbindung vermessen, die als Verunreinigung im Reaktionsprodukt enthalten war, und daher sind alle Schlussfolgerungen hinfällig, die sich aus diesen Daten ergeben, obgleich einige goldhaltige Reaktionsprodukte in hohen Ausbeuten erhalten wurden. Aus diesem Grund ziehen die Autoren die Zuschrift zurück, und sie entschuldigen sich bei den Lesern der *Angewandten Chemie*. Sie bedanken sich bei Prof. H. Schmidbaur, der sie auf diesen Sachverhalt aufmerksam gemacht hat.

31. Oktober 2006

Jahn–Teller Distortion in Gold

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$[NEt_4][AuCl_2][AuCl_3]$: Solid-State Evidence of Essentially Y-Shaped Jahn–Teller-Distorted $AuCl_3$**

Kevin R. Flower, Robin G. Pritchard, and Alan T. McGown*

Gold halides are of considerable interest to computational and synthetic chemists alike owing to their interesting structural and bonding characteristics.[1–4] Of particular interest is the first-order Jahn–Teller distortion of the AuX_3 molecules (X = F, Cl, Br, I). Calculations have shown that the D_{3h} trigonal-planar structure is not the lowest-energy structure for AuL_3. Rather it distorts to T-, Y-, or even L-shaped geometries.[1,5] Looking at the frontier orbitals for the AuL_3 d^8 system with $D_{3h}(^1E')$ symmetry, there are two electrons in a doubly degenerate e′ orbital. Bending of the AuL_3 system breaks the degeneracy, thereby causing the formation of a doubly occupied b_2 (HOMO) and an empty a_1 (LUMO) orbital for a distorted $C_{2v}(^1A_1)$ symmetry: a first-order Jahn–Teller effect.[5]

This T-shaped geometry has been found to be the minimum for the Jahn–Teller surface of AuF_3, $AuCl_3$, and $AuBr_3$, with a Y-shaped geometry as the high-lying transition state between two T-shaped geometries such that the D_{3h} geometry is a second-order saddle point (Mexican hat with three bumps). Calculations have also been carried out on AuH_3[5] and $Au(CH_3)_3$,[6] and they also predict T-shaped ground-state geometries. Experimental data is available[3] for AuF_3 (electron diffraction) and shows clearly that it has T-shaped geometry in the gas phase. In a recent study combining matrix-isolation electronic absorption, IR, and AuL_3-edge EXAFS, it was shown that $AuCl_3$ also has a T-shaped geometry as a result of Jahn–Teller distortion.[7] This observation is consistent with the suggestion of Schultz and Hargittai that AuF_3 and $AuCl_3$ are static Jahn–Teller systems.[1] The related[1,4] molecules AuX_3 (X = Br and I) were found to have relatively flat potential-energy surfaces, and the energetic gain from Jahn–Teller distortion is small for these dynamic systems.

The solid-state structures of $[Au_2X_6]$ (X = F, Cl, Br) have also been described.[5,8–10] In all cases the gold center is found in the expected square-planar arrangement for a late-transition-metal d^8 cation.[11] For $[Au_2F_6]$, however, the square-planar $\{AuF_4\}$ units are linked by μ-F bridges in *cis* positions, thus affording an extended helical structure.[8] These solid-state intermolecular interactions are 0.7 Å longer than those observed in the $[Au_2F_6]$ moiety. The crystal and molecular structure of the mixed Au^I/Au^{III} compound $Cs_2[AuCl_2][AuCl_4]$ has also been described, and it contains a square-planar Au^{III} center with a linear Au^I center as expected.[12] Herein, we report the solid-state structure of $[NEt_4][AuCl_2][AuCl_3]$, which contains essentially Y-shaped $AuCl_3$, thus affording the first solid-state evidence for first-order Jahn–Teller distortion in $AuCl_3$.

Treatment of $[NEt_4][AuCl_4]$ with $Hg(C_6H_4\text{-}4\text{-}OMe)_2$ in acetonitrile afforded, after recrystallization, $[NEt_4][AuCl_2][AuCl_3]$ (**1**) and 4,4′-$(MeO)_2$-$C_{12}H_8$. Recrystallization of **1** from $NCMe/CH_2Cl_2$ at 277 K afforded crystals of **1** suitable for an X-ray diffraction study (Figure 1). Of particular note are the non-square-planar Au^{III} chloride fragment and the shorter Au^I–Cl bonds (av 2.322 Å) versus the Au^{III}–Cl bonds (av 2.441 Å). The latter is a direct result of relativistic effects, which dominate the chemistry of gold.[13] This property mirrors the shorter Au^I–Cl bond length observed in the crystallographically determined structure of $Cs_2[AuCl_2][AuCl_4]$.[9] The structure of the $AuCl_3$ fragment in **1** has a geometry intermediate (**B**) between the trigonal planar (D_{3h}, **A**) and T-shaped (C_{2v}, **C**) geometries (Figure 2).

[*] Dr. K. R. Flower, Dr. R. G. Pritchard
School of Chemistry
University of Manchester
Sackville Street, Manchester (UK)
Fax: (+44) 161-306-4459
E-mail: k.r.flower@manchester.ac.uk
Prof. A. T. McGown
Drug Discovery Unit
University of Salford
Frederick Street Campus, Salford (UK)

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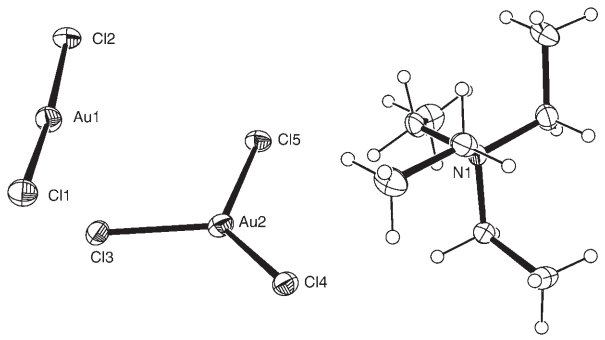

Figure 1. ORTEP representation of the molecular structure of **1**. Thermal ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.311(4), Au1-Cl2 2.334(4), Au2-Cl3 2.452(4), Au2-Cl4 2.454(4), Au2-Cl5 2.417(4); Cl1-Au1-Cl2 170.53(11), Cl3-Au2-Cl4 118.21(13), Cl3-Au2-Cl5 111.42(13), Cl4-Au2-Cl5 127.89(13).

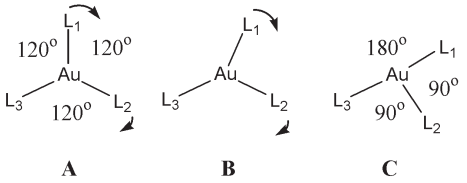

Figure 2. Pictorial representation of the bending in the AuL_3 fragments: **A** trigonal-planar; **B** Y-shaped; **C** T-shaped.

The structural features of the $[NEt_4][AuCl_2]$ portion of the structure are comparable to those that have been previously crystallographically determined for $[NEt_4][AuCl_2]$.[14]

By increasing the acceptable bonding radius of Cl to 1.20 Å from 0.99 Å, it becomes evident that Cl4 asymmetrically bridges two gold centers (Au2–Cl4 2.454(3) Å, Au2–Cl4_2 2.822(3) Å). This bridging affords an $\{Au_2Cl_6\}$ unit (Figure 3), which clearly differs from the previously reported structure of $[Au_2Cl_6]$ in which the Au^{III} atoms display the expected square-planar geometry with symmetric Au-Cl-Au bridges (Au–Cl 2.334(10) Å). The closest nonbonding approach in the square-planar structure is 3.487(10) Å. Schwerdtfeger et al. suggested[5] that the dimerization of the $AuCl_3$ fragments to give $[Au_2Cl_6]$ could easily be visualized as the bridging of equatorial ligands in the C_{2v}-symmetric T-shaped Jahn–Teller-distorted $AuCl_3$ fragments. The dimer

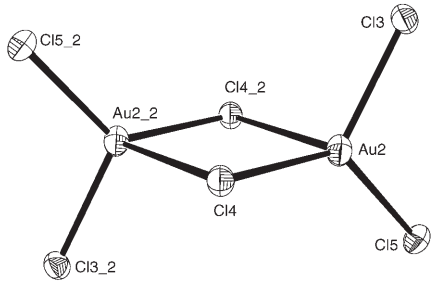

Figure 3. ORTEP representation of the $\{Au_2Cl_6\}$ fragment in **1**. Selected bond lengths [Å] and angles [°]: Au2-Cl4 2.454(4), Au2-Cl4_2 2.822(3); Cl4-Au2-Cl4_2 85.53(10), Au2-Cl4-Au2_2 94.47(10).

reported here can be visualized in a similar fashion in that two essentially Y-shaped fragments sit tail-to-tail, one on top of the other. The overall geometry is now closer to that observed for other $[M_2X_6]$ systems, which are described as two tetrahedra sharing one edge.[15]

Upon increasing further the acceptable covalent radius of Cl to 1.30 Å, an additional weak interaction between Cl3 and Au1 is observable (2.907(4) Å, Figure 4). A similar bridging

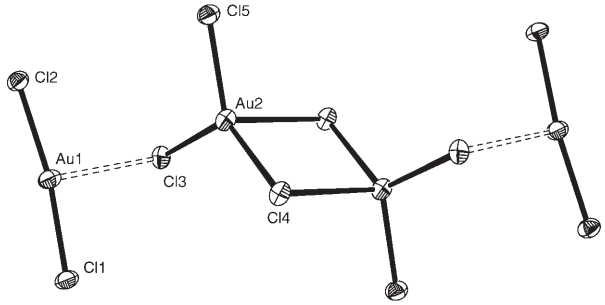

Figure 4. ORTEP representation of the $[AuCl_2][Au_2Cl_6][AuCl_2]$ chain in **1**. Selected bond lengths [Å] and angle [°]: Au1-Cl3 2.907(4), Au2-Cl3 2.452(4); Au2-Cl3-Au1 103.17(13).

interaction (Cl5–Au1 3.208(5) Å, Au2-Cl5-Au1 95.81(13)°) is also evident and is within the sum of the accepted van der Waals radii.[16] Finally, the extended structure is shown in Figure 5 and is best considered as a chain of repeating {-Cl-

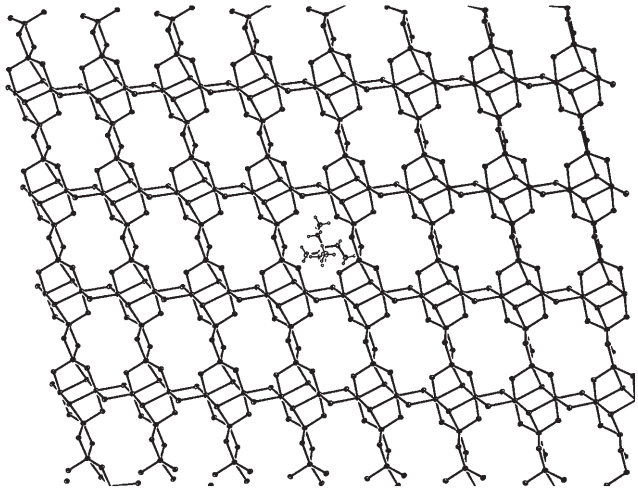

Figure 5. ORTEP representation of the extended structure of **1**.

Au^{III}-Cl-Au^{III}-Cl-Au^{I}-} units running from top to bottom of the diagram and a chain of alternating {-Cl-Au^{I}-Cl-} units running from right to left that creates channels in the structure that are occupied by the $[NEt_4]^+$ countercations. In the {-Cl-Au^{I}-Cl-} chain there are two possible $Au^{I}\cdots Au^{I}$ interactions. They are found to have separations of 4.104(12) and 4.210(14) Å and are longer than the Au2···Au2_2 separation of 3.881(16) Å. This finding means that there are no aurophilic interactions in this structure,[17] the most likely

reason being the octahedral coordination geometry at the Au^I atom in the extended structure.

In conclusion, the solid-state structure of **1** gives the first solid-state evidence for Jahn–Teller distortion in a structure containing $AuCl_3$. The distortion observed is more representative of the Y-shaped transition state, in which two Au–X bonds are 120° or greater (127°, 118°, 111° for **1**), that is predicted by theoretical calculations than the expected T-shaped geometry with idealized angles of 180°, 90°, and 90°. In the extended structure there is clear evidence for asymmetric bridging of two $AuCl_3$ units to give an $\{Au_2Cl_6\}$ unit that does not show the expected square-planar geometry at the d^8 gold(III) center, but is more representative of other $[M_2X_6]$ systems.

Experimental Section

1 (Caution! Use of an organomercurial compound): $Hg(C_6H_4$-4-$OMe)_2$ (89 mg, 0.213 mmol) was added to a solution of $[NEt_4][AuCl_4]$ (100 mg, 0.213 mmol) in NCMe (25 mL) with continuous stirring at 273 K. After 3 h the solution was filtered through celite, and the solvent was removed in vacuo. Extraction of the crude product with hexane afforded 4,4′-$(MeO)_2$-$C_{12}H_{10}$ (42 mg, 92 %). Recrystallization of the remaining material from $NCMe/CH_2Cl_2$ (1:3) afforded **1** (48 mg, 75 %).

Crystallography: A suitable crystal of **1** was grown from $NCMe/CH_2Cl_2$ (1:3) at 277 K. The X-ray diffraction data were collected at 200 K with a Nonius Kappa CCD 4-circle diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); CCD rotation images, thick slices, scans performed to $2\theta_{max} = 52°$.

Crystal data for $[C_8H_{20}N]^+[Au_2Cl_5]^-$, $C_8H_{20}Au_2Cl_5N$, $M_r = 701.43$, crystal dimensions $0.1 \times 0.1 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.2871(1)$, $b = 10.4086(2)$, $c = 10.9548(2)$ Å, $\alpha = 105.697(1)$, $\beta = 96.636(1)$, $\gamma = 108.756(1)°$, $V = 839.85(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.774$ Mg m^{-3}, $\mu = 18.221$ mm^{-1}, $F(000) = 636$, 13 366 reflections collected, 3262 unique [$R_{int} = 0.082$], 2569 [$I > 2\sigma(I)$], Lp and absorption corrections (semiempirical from equivalents, max/min transmission 0.463, 0.263). The structure was solved by direct methods using SHELXS-97[18] and refined against F^2 using SHELXL-97 (142 parameters). $wR_2 = 0.1654$ (all data), $R_1 = 0.0589$ [$I > 2\sigma(I)$]. Difference map max/min 3.36, −2.78 e Å^{-3}. CCDC-608090 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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