Deprotonated ethylenethiourea as a ligand in an unusual tetrameric gold(I) complex†

Peter G. Jones* and Steffi Friedrichs

Institut für Anorganische und Analytische Chemie, Technical University of Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: p.jones@tu-bs.de

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The product of the reaction between $[(\mathrm{etu})_2\mathrm{Au}]^+\mathrm{Cl}^-$ (etu = imidazolidine-2-thione) and aqueous sodium hydroxide, previously described as $\{(\mathrm{etu})\mathrm{Au}\}_2\mathrm{O}$, is shown by X-ray analysis to be a tetramer with four gold(I) centres and four deprotonated etu ligands acting as *N*,*S*-donors.

Ethylenethiourea [imidazolidine-2-thione (etu)] is a well known ligand in the chemistry of gold(I); complexes such as $[(\mathrm{etu})_2\mathrm{Au}]\mathrm{Cl}\cdot\mathrm{H_2O}$ were described as long ago as 1928.[1] Also reported[1] was $\{(\mathrm{etu})\mathrm{Au}\}_2\mathrm{O}$, apparently the product of the reaction between $[(\mathrm{etu})_2\mathrm{Au}]\mathrm{Cl}$ and aqueous sodium hydroxide. In the light of current knowledge, this complex would be unexpected because of the extremely low affinity of gold(I) centres for oxide ligands; as far as we are aware, there is no established example of such a complex. We have recently begun a study of hydrogen bonding in etu complexes of gold(I),[2] in the course of which we decided to re-examine the previous report.

The reaction between $[(\mathrm{etu})_2\mathrm{Au}]\mathrm{Cl}$ and aqueous alkalis is not difficult to reproduce; it leads immediately to a white precipitate, which is however practically insoluble in all common solvents. In such cases the slow diffusion of reacting solutions may lead to crystalline material; the careful layering of the three phases aqueous potassium hydroxide (bottom), ethyl acetate (centre) and ethanolic $[(\mathrm{etu})_2\mathrm{Au}]\mathrm{Cl}$ (top) indeed led to single crystals, albeit extremely small. An X-ray structure determination did however prove possible, exploiting the greater sensitivity of area detector technology.‡

The structure is shown in Fig. 1. It is a tetramer $[\mathrm{Au}(\mathrm{etu} - \mathrm{H})]_4$, where (etu − H) indicates an ethylenethiourea deprotonated at one nitrogen atom.§ The ligands coordinate through S and the deprotonated N atom, and there are two differently coordinated types of gold centre. Gold atoms Au2 and Au3 lie on twofold axes $\frac{1}{2},\frac{1}{2}, z$ and are linearly coordinated by two nitrogen atoms [Au2–N12 2.04(1), Au3–N22 1.97(1) Å], whereas Au1 lies on a general position and is coordinated by two sulfur atoms [Au1–S1 2.284(4), Au1–S2 2.304(4) Å] in a distorted linear geometry [S–Au–S 169.8(2)°]. As far as we are aware, only one other complex of (etu − H) is known: $[\mathrm{Mo_2(py)_2(O_2CBu^t)_3(etu - H)}]$.[3]

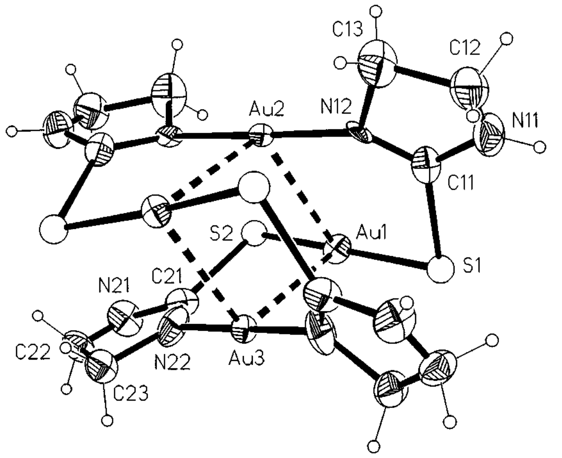

Fig. 1 Structure of the tetramer $[\mathrm{Au}(\mathrm{etu} - \mathrm{H})]_4$ in the crystal. Only the asymmetric unit is numbered. Ellipsoids represent 50% probability levels; H and S atom radii are arbitrary (see text).

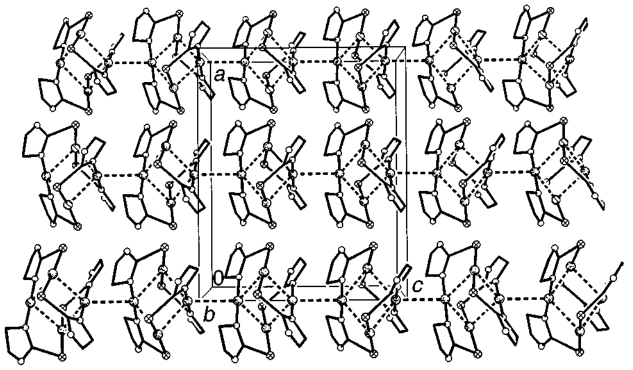

Fig. 2 Packing diagram of $[\mathrm{Au}(\mathrm{etu} - \mathrm{H})]_4$, showing the formation of chains of tetramers parallel to the *z* axis. Au···Au contacts are indicated by dashed lines. H atoms are omitted.

The tetramer contains a 16-membered ring comprising the gold atoms, all N and S donor atoms, and one C atom of each (etu − H) ligand. Within this ring, the gold atoms are connected *via* short Au···Au contacts Au1···Au2 2.972(1) and Au1···Au3 2.974(1) Å to form a rhombus with angles of 71.28(2)° at Au1 and 108.79(7)° at Au2. A similar arrangement was observed in the gold(I) thioacetate tetramer $[\mathrm{Au(MeCS_2)}]_4$.[4] In the current structure, the tetramers are further linked into chains parallel to the *z* axis by contacts Au2···Au3′ 3.176(1) Å (Fig. 2). The nonbonded S···N distances are S2···N12′ 3.23 and S1···N22′ 3.24 Å.

The existence of oxide complexes of Au(I) thus still remains to be demonstrated, whereas the (etu − H) ligand has been found at gold for the first time. Investigations of the reactivity of the (etu − H) tetramer are in progress.

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Notes and references

‡ X-Ray structure determination: A colourless needle (*ca.* 0.1 × 0.02 × 0.01 mm) was mounted in inert oil on a glass fibre. Data were measured using Mo-Kα radiation on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were based on multiple scans (program SADABS). Structure solution and refinement proved difficult because of pseudo-symmetry; the gold atoms simulate an additional pseudo-mirror plane. The sulfur atoms were refined isotropically because the two components of the double image thus generated are closely adjacent. Otherwise, the structure was refined [as a racemic twin with components 0.54(2): 0.46(2)] anisotropically on F^2 using all reflections (program SHELXL-97[5]). Hydrogen atoms were placed in calculated positions (assuming planarity at nitrogen) and refined using a riding model. An extensive set of restraints

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† Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday.

were employed to improve stability of refinement. In view of the severe pseudo-symmetry, bond lengths should be interpreted with caution.

Crystal data: $C_{12}H_{20}Au_4N_8S_4$, M = 794.98, orthorhombic, space group *Iba*2, a = 16.1973(9), b = 10.3143(6), c = 13.2818(7) Å, V = 2218.9(2) Å^3, Z = 4, μ = 26.7 mm^{-1}, T = −130 °C, Bruker SMART 1000 CCD diffractometer, 11373 reflections to $2\theta_{max}$ 56°, 2759 unique, 119 parameters, 154 restraints, $wR2$ = 0.081, $R1$ = 0.032, S = 1.03, max. $\Delta\rho$ 2.26 e Å^{-3}.

CCDC 182/1293. See http://www.rsc.org/suppdata/cc/1999/1365/ for crystallographic files in .cif format.

§ The chemical analysis was satisfactory: found. (calc.) for $C_{12}H_{20}Au_4N_8S_4$; C, 11.91 (12.09); H, 1.49 (1.69); N, 9.26 (9.40); S, 10.79 (10.75)%. It is instructive to compare these values with those quoted in 1928 for $C_6H_{12}Au_2ON_4S_2$:[1] C, 11.45 (11.7); H, 2.1 (2.0); N, 9.3 (9.1); S, 10.5 (10.4); Au, 64.8 (64.2)%.

1 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1928, 143.
2 P. G. Jones and S. Friedrichs, manuscript in preparation.
3 R. H. Cayton, M. H. Chisholm, E. F. Putilina and K. Folting, *Polyhedron*, 1993, **12**, 2627.
4 O. Piovescana and P. F. Zanazzi, *Angew. Chem. Int. Ed. Engl.*, 1980, **7**, 579.
5 G. M. Sheldrick, SHELXL-97, a program for refining crystal structures, University of Göttingen, Germany, 1997.

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