Crystal and molecular structure of bis(N,N-di-*n*-butyldithiocarbamato)-gold(III) bis(1,2-dicyanoethene-1,2-dithiolato)aurate(III)

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Abstract

The crystal and molecular structure of bis(N,N-di-*n*-butyldithiocarbamato)gold(III) bis(1,2-dicyanoethene-1,2-dithiolato)aurate(III), $\text{Au}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2\text{Au}[\text{S}_2\text{C}_2(\text{CN})_2]_2$, has been determined from a single-crystal X-ray diffraction study. The monoclinic cell, space group $P2_1/c$, with $a = 9.930(3)$, $b = 12.517(3)$, $c = 15.632(3)$ Å and $\beta = 110.46(3)^\circ$, contains two formula units. Three-dimensional intensity data, up to $\theta = 35^\circ$ were collected on an automatic diffractometer. Atomic parameters were refined by full-matrix least-squares methods to a conventional R value of 0.04 for 1874 independent non-zero reflections. The structure consists of bis(di-*n*-butyldithiocarbamato)gold(III) cations and bis(1,2-dicyanoethene-1,2-dithiolato)aurate(III) anions. In both ions, the gold atom is in planar coordination with four sulphur atoms, the Au—S bond lengths being 2.333(4) and 2.337(4) Å in the cation and 2.312(4) and 2.306(5) Å in the anion.

Introduction

During the work on the redox properties of dithiocarbamato and dithiolato complexes of transition metals at the Department of Inorganic Chemistry of this University, two complexes of composition $\text{Au}(\text{dtc})(\text{mnt})$, ($\text{dtc} = \text{N,N-di-}n\text{-butyldithiocarbamate}$, $\text{mnt} = \text{maleonitriledithiolate} \equiv 1,2\text{-dicyanoethene-1,2-dithiolate}$) were synthesised (van der Linden, 1971).

One complex appeared to be the ionic compound $\text{Au}(\text{dtc})_2^+ \text{Au}(\text{mnt})_2^-$, whereas the other one is the mixed dithiocarbamato-dithiolato complex, $\text{Au}(\text{dtc})(\text{mnt})$. To supply further information for discussion of the bonding in square-planar complexes, structure analysis of both compounds was initiated. In this paper the structure of the ionic species is reported; structural studies of the mixed ligand complex are in progress.

Experimental

The complex $\text{Au}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2\text{Au}[\text{S}_2\text{C}_2(\text{CN})_2]_2 = \text{Au}(\text{dtc})_2\text{Au}(\text{mnt})_2$ crystallizes as well-formed brown crystals elongated along a . Preliminary Weissenberg photographs showed the crystals to be monoclinic, with space group $P2_1/c$. From Pt-calibrated Weissenberg photographs around a and

b, using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), application of a least-squares procedure yielded the unit cell dimensions: $a = 9.930(3)$, $b = 12.517(3)$, $c = 15.632(3) \text{ \AA}$, $\beta = 110.46(3)^\circ$, $V_c = 1820(1) \text{ \AA}^3$. The calculated density of 1.98 g cm^{-3} with $Z = 2$ agrees fairly well with the value of $2.02(2) \text{ g cm}^{-3}$, from pycnometric measurements. A crystal of approximate dimensions $0.20 \times 0.15 \times 0.15 \text{ mm}^3$, was mounted with *a* along the φ -axis of a Nonius automatic diffractometer. Intensity data were measured with Zr-filtered Mo radiation (linear absorption coefficient $\mu = 87.8 \text{ cm}^{-1}$) using the moving counter-moving crystal method with a scan speed of $0.3^\circ/\text{min}$. After every fifteen reflexions, a reference reflexion was measured to detect and allow correction to be made for slow fluctuations in the primary beam. Of the 7990 independent reflexions theoretically attainable within the limit $\theta = 35^\circ$, 1874 reflexions were measured above background. Absorption corrections were calculated according to the Busing & Levy (1957) procedure, using $7 \times 7 \times 7$ volume components and six accurately-located boundary planes.

Structure determination

The reflexions hkl with $h = 2n$ and $k + l = 2n$ are very strong relative to the remaining reflexions. The gold atoms were therefore placed at the special positions 000 , $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$. A Patterson synthesis showed sixteen Au—S vectors around the origin. Based upon five possible sites indicated by the Patterson synthesis, several trial structures were tested but all failed to refine. A procedure was then developed for applying direct methods to centrosymmetric structures containing heavy atoms (Beurskens & Noordik, 1971).

A modified Wilson plot was calculated to obtain approximate scale and overall isotropic temperature factors of the gold atoms and of the light atoms. The calculated contributions of the gold atoms were subtracted from the observed structure factors of the 1337 'strong' reflexions hkl ($h = 2n$, $k + l = 2n$) to obtain the contributions F_L of the remaining atoms. As the sign of the structure factors of these 'strong' reflexions is determined by the gold atoms, both the magnitude and sign of F_L for these reflexions are established. The observed structure factors of the remaining 538 'weak' reflexions do not have any contribution from the gold atoms (assuming the same spherically-symmetrical electron-density distribution at the Au(1) and Au(2) sites) and, therefore, only the magnitude $|F_L|$ of these reflexions is known: $|F_L| = |F_{obs}|$. The structure factors of the 'remainder structure' (i.e. total structure excluding Au atoms) were converted to normalized structure factors E_L and the well-known Sayre-Zachariasen-Cochran triple product sign relationship $S_{h+h'} \sim S_h \cdot S_{h'}$ was applied to reflexions with $|E_L| > 1.3$, to find the signs of the 'weak' reflexions.

A Fourier synthesis calculated with 549 reflexions (365 'strong' reflexions, 2 'weak' reflexions to fix the origin and 182 reflexions determined by the sign relationship) revealed the positions of all of the light atoms of the structure, except the hydrogen atoms. The structure factor calculation gave an *R* value of 0.12. Refinement with anisotropic temperature factors for all atoms reduced this to 0.06. A difference Fourier synthesis, using terms for which $\sin \theta/\lambda < 0.35 \text{ \AA}^{-1}$, showed all eighteen hydrogen atoms at expected positions. As the difference Fourier synthesis did not allow accurate location of the hydrogen atoms, they were placed at calculated positions (Table 2) (allowing rotation of the methyl groups to give the best fit with the difference Fourier synthesis) and allocated *B* values of $4.0 \text{ \AA}^2$. Several more cycles of full-matrix anisotropic least-squares refinement with fixed hydrogen parameters reduced *R* to a final value of 0.04 for 1874 observed reflexions. The separate final *R* values for the 'strong' reflexions and for the 'weak' reflexions are 0.036 and 0.068 respectively. In the last cycle, the changes in all parameters were only a fraction of the standard deviations. The function that was minimized was $w(|F_o| - |F_c|)^2$. The weight *w* for each reflexion was calculated according to $w = 1/(a|F_o| + b)$ with $a = -0.47$ and $b = 40$ for $F_o < 45$, $a = 0.013$ and $b = 18$ for $45 < F_o < 120$ and $a = 0.30$ and $b = -17$ for $F_o > 120$; these coefficients were based upon a plot of $(|F_o| - |F_c|)^2$ against $|F_o|$. The atomic scattering factors used were those of Au⁺, S, C, N and H with those for Au⁺ corrected for anomalous scattering ($\Delta f'$, $\Delta f''$), using data from the *International Tables for X-ray Crystallography*.

Table 1. *Final atomic positional and thermal parameters for Au(dtc)₂Au(mnt)₂*

The esd result from the least-squares refinement. The expression for the temperature factor is:

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl).$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au(1)	0	0	0	0.0110(1)	0.0046(1)	0.0030(1)	-0.0018(1)	0.0027(1)	-0.0003(1)
Au(2)	$\frac{1}{2}$	0	0	0.0083(1)	0.0049(1)	0.0037(1)	0.0005(1)	0.0022(1)	0.0004(1)
S(1)	0.0522(5)	0.1567(3)	-0.0630(3)	0.0147(6)	0.0059(3)	0.0029(2)	-0.0025(4)	0.0023(3)	-0.0004(2)
S(2)	0.1391(5)	0.1017(4)	0.1250(3)	0.0146(6)	0.0060(3)	0.0030(2)	-0.0027(3)	0.0028(3)	-0.0003(2)
S(3)	0.5354(5)	0.1045(4)	0.1280(3)	0.0122(6)	0.0068(3)	0.0039(2)	0.0000(4)	0.0031(3)	-0.0000(2)
S(4)	0.6454(5)	0.1115(4)	-0.0471(3)	-0.0135(6)	0.0064(3)	0.0056(2)	-0.0013(4)	0.0049(3)	-0.0004(2)
N(1)	0.213(1)	0.288(1)	0.069(1)	0.010(2)	0.005(1)	0.003(1)	0.000(1)	0.002(1)	-0.000(1)
N(2)	0.741(2)	0.342(2)	0.243(1)	0.028(4)	0.009(1)	0.006(1)	-0.003(2)	0.002(2)	-0.001(1)
N(3)	0.861(2)	0.354(1)	0.023(1)	0.015(3)	0.009(1)	0.007(1)	-0.004(2)	0.003(1)	0.000(1)
C(1)	0.149(2)	0.198(1)	0.048(1)	0.010(2)	0.005(1)	0.003(1)	-0.001(1)	0.004(1)	0.000(1)
C(2)	0.214(2)	0.365(1)	-0.003(1)	0.014(3)	0.005(1)	0.004(1)	-0.001(1)	0.004(2)	0.001(1)
C(3)	0.346(2)	0.347(1)	-0.032(1)	0.011(2)	0.007(1)	0.004(1)	-0.002(1)	0.003(1)	-0.001(1)
C(4)	0.337(2)	0.419(2)	-0.111(1)	0.011(2)	0.010(2)	0.005(1)	0.001(2)	0.004(1)	0.002(1)
C(5)	0.471(2)	0.409(2)	-0.138(1)	0.011(2)	0.011(1)	0.003(1)	-0.001(2)	0.002(1)	0.000(1)
C(6)	0.296(2)	0.315(1)	0.166(1)	0.010(2)	0.006(1)	0.002(1)	-0.001(1)	0.000(1)	-0.001(1)
C(7)	0.206(2)	0.367(1)	0.215(1)	0.015(3)	0.007(1)	0.004(1)	0.001(2)	0.003(1)	-0.000(1)
C(8)	0.153(2)	0.479(1)	0.185(1)	0.014(2)	0.007(2)	0.004(1)	-0.001(1)	0.004(1)	-0.001(1)
C(9)	0.069(2)	0.527(1)	0.241(1)	0.013(2)	0.009(2)	0.005(1)	-0.001(1)	0.002(1)	-0.003(1)
C(10)	0.656(2)	0.200(1)	0.114(1)	0.011(2)	0.005(1)	0.005(1)	0.001(1)	0.002(1)	0.001(1)
C(11)	0.670(2)	0.205(1)	0.042(1)	0.008(2)	0.005(1)	0.004(1)	0.000(1)	0.002(1)	0.001(1)
C(12)	0.701(2)	0.277(2)	0.187(1)	0.014(3)	0.007(1)	0.006(1)	0.000(1)	0.002(1)	0.001(1)
C(13)	0.791(2)	0.287(1)	0.033(1)	0.012(2)	0.005(1)	0.006(1)	0.001(1)	0.003(1)	-0.000(1)

Table 2. *Unrefined hydrogen atom positional parameters (*B* = 4.0 Å²)*

The first index identifies the parent carbon atom.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(21)	0.21	0.45	0.02
H(22)	0.11	0.36	-0.07
H(31)	0.35	0.26	-0.06
H(32)	0.45	0.36	0.02
H(41)	0.34	0.50	-0.09
H(42)	0.24	0.41	-0.17
H(51)	0.46	0.47	-0.18
H(52)	0.56	0.40	-0.08
H(53)	0.46	0.33	-0.18
H(61)	0.38	0.37	0.17
H(62)	0.35	0.24	0.21
H(71)	0.25	0.37	0.29
H(72)	0.10	0.32	0.20
H(81)	0.09	0.48	0.11
H(82)	0.25	0.53	0.19
H(91)	0.13	0.48	0.30
H(92)	-0.04	0.49	0.22
H(93)	0.06	0.61	0.24

Calculations were performed on an IBM 360/50 computer, using programs written by Busing, Martin & Levy (1962), Johnson (1965), Ahmed & Pippy (1968) and data reduction programs written at this laboratory. Programs for the application of direct methods, written by Dewar & Stone (1966) were modified by one of the authors (J.H.N.) for the special procedure described in this paper.

Description and discussion

Interatomic distances and angles, computed from the parameters of Table 1, are given in Fig. 1. Projections of the structure along *b* and *c* are presented in Fig. 2 and Fig. 3 respectively. The $\text{Au}(\text{dte})_2^+$ and $\text{Au}(\text{mnt})_2^-$ ions are illustrated in Fig. 4.

Fig. 1. Geometry of $\text{Au}(\text{dte})_2^+$ (top) and $\text{Au}(\text{mnt})_2^-$ (bottom) with esd in parentheses.

In the anion, as well as in the cation, the gold atom is situated at a centre of symmetry and is in planar coordination with four sulphur atoms. Anions and cations alternate in strings in the direction of the *a* axis, with an angle of 36.3° between the coordination planes of neighbouring ions. Parallel strings are related by two-fold screw-axes. No interionic contacts less than those expected from van der Waals radii occur.

In the $\text{Au}(\text{dte})_2^+$ cation, the $\text{S}(1)-\text{Au}(1)-\text{S}(2)$ angle is $75.0(2)^\circ$ and the two symmetry independent Au—S bond lengths are $2.333(4)$ and $2.337(4)$ Å. The ion is nearly planar, except for the butyl chains. The equation of the least-squares plane through $\text{Au}(1)$, $\text{S}(1)$, $\text{S}(2)$ and $\text{N}(1)$ is given by: $0.9050X - 0.4224Y - 0.0515Z = 0$. No atoms deviate by more than one standard deviation from this plane. The distances of $\text{C}(2)$ and $\text{C}(6)$ from this plane are $0.01(2)$ and $0.05(2)$ Å respectively. Bond lengths and angles in the cation are in close agreement with those found in other structures

containing the $\text{Au}(\text{dtc})_2^+$ ion (Beurskens, Blaauw, Cras & Steggerda, 1968; Beurskens, Cras & van der Linden, 1970; Cras, Noordik, Beurskens & Verhoeven, 1971).

The coordination of the gold atom in the $\text{Au}(\text{mnt})_2^-$ anion is nearly square-planar, the $\text{S}(3)\text{—Au}(2)\text{—S}(4)$ angle being $90.7(2)^\circ$ and the two Au—S bond lengths being $2.312(4)$ and $2.306(5)$ Å. The intra-ligand $\text{S}(3)\text{—S}(4)$ distance and the inter-ligand $\text{S}(3)\text{—S}(4')$ distance are $3.284(7)$ and $3.246(7)$ Å respectively. The equation of the least-squares plane through all atoms of the anion

Fig. 2. Projection of the structure along b . Gold atoms are on centres of symmetry and two-fold screw axes are indicated. White ions are at $y = 0$ and black ions are at $y = \frac{1}{2}$.

is given by: $-0.6581X + 0.5607Y - 0.5026Z + 3.2673 = 0$. The largest distance from this plane, $-0.09(2)$ Å, is found for the nitrogen atom N(2).

Bond lengths and angles in the anion agree to within one or two standard deviations with those found in the comparable $\text{Au}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2^-$ ion (Enemark & Ibers, 1968) except for possible significant differences in the Au—S distances and S—Au—S angle. Similar differences are found in comparable Co and Ni complexes as can be seen in Table 3. From the available data it would appear that the S—metal—S angle in the dithiolato system is more sensitive to a change of substituents than are the bond lengths.

Fig. 3. Projection of the structure along c . Only one string of ions (at $z = 0$) is given.

Fig. 4. View of the $\text{Au}(\text{dte})_2^+$ ion (top) and the $\text{Au}(\text{mnt})_2^-$ ion (bottom), illustrating the thermal anisotropy.

The significant difference in Au—S bond lengths in the cation and the anion, again shows that metal-ligand π -bonding is more substantial in complexes of 1,2-dithiolato ligand systems than it is in complexes of 1,1-dithiolato ligand systems (Eisenberg, 1970).

Table 3. *Interatomic distances and angles* within the ethene-1,2-dithiolato ligands of some transition-metal complexes*

		M—S (Å)	S—C (Å)	C=C (Å)	S—M—S (°)	Ref.
π -C ₅ H ₅ —CoS ₂ C ₂ R ₂	R=CF ₃	2.08(1)	1.74(5)	1.48(5)	92.2(2)	<i>a</i>
	R=CN	2.117(2)	1.702(6)	1.364(10)	93.2(1)	<i>b</i>
Ni(S ₂ C ₂ R ₂) ₂ ⁻	R=CF ₃	2.136(3)	1.70(1)	1.40(2)	91.4(1)	<i>c</i>
	R=CN	2.147(1)	1.715(2)	1.355(5)	92.3(1)	<i>d</i>
Au(S ₂ C ₂ R ₂) ₂ ⁻	R=CF ₃	2.288(4)	1.77(1)	1.30(2)	89.7(2)	<i>e</i>
	R=CN	2.309(4)	1.75(1)	1.35(2)	90.7(2)	<i>f</i>

* Average of symmetry-independent values.

(a) Baird & White (1966)

(b) Churchill & Fennessey (1968).

(c) Wing & Schlupp (1970).

(d) Fritchie (1966).

(e) Enemark & Ibers (1968).

(f) This work.

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