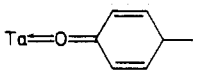
Table VI. Average Ring Bond Distances for Phenoxides in II (Å)

	C–O	C–C (o)	C–C (m)	C–C (p)
terminal	1.344 (20)	1.378 (22)	1.368 (21)	1.365 (23)
bridging	1.418 (15)	1.349 (20)	1.384 (23)	1.321 (27)

to the terminal and bridge cresoxides, respectively. There was only one methyl resonance in the ^{13}C NMR of II.

The ^1H NMR of II had three methyl resonances with relative areas of 1:2:2, further consistent with a static solution structure. An unusual feature of the ^1H NMR of both I and II was the appearance of an upfield doublet peak at ca. δ 6.00. This feature has been observed in the ^1H NMR spectra of complexes in which an ortho-metalated group is present. For instance, $HCo(P(OPh)_3)_4$ has a single multiplet resonance at ca. δ 6.9 whereas $(PhO)_2POC_6H_4Co(P(OPh)_3)_3$ has multiplets at δ 7.20, 6.46, 6.79, and 6.38. This effect has been seen in several other systems.[10]

Examination of the nonbonded distances in II shows that the closest ortho carbon–Ta distance is 3.697 Å[15] (Ta–C(30)). Thus, no ortho metalation exists in II. (See Figure 2 in supplementary material, stereoview of II.) The upfield chemcial shift is consistent with the notion that the cresoxide ligands are engaged in multiple bonding to tantalum. Removing electron density from the ring would be consistent with the observed upfield shift in the NMR, i.e., the cresoxide ligand is becoming quinone-like:



The distances about the cresoxide rings further support the notion of multiple M–O bonding. The expectation, if M–O multiple bonding occurs, is that there should be shortening of the C–O and C–C bonds with a lengthening of the ortho and para C–C bonds relative to an unperturbed phenoxide. One can use the bridging ligand as an internal reference for atom distances as a cresoxide not engaged in M–O multiple bonding. In Table VI, the average C–O and C–C (ortho, meta, and para) distances are shown for bridging vs. terminal cresoxides in II. There is large scatter in the data used to generate Table VI. The trends are that the predicted shortening of the C–O and C–C (meta) bonds was observed for the terminal vs. bridging ligands. Likewise, the expected C–C (ortho and para) lengthening of terminal vs. bridging is seen.

Registry No. I, 75888-51-6; II, 94234-92-1.

Supplementary Material Available: A stereoview of II (Figure 2) and listings of observed and calculated structure factors (Table VII), anisotropic temperature factors (Table VIII), and hydrogen coordinates (Table IX) (21 pages). Ordering information is given on any current masthead page.

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Gold Dithiocarboxylates

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The first dithiocarboxylato derivatives of gold have been obtained. The compounds have stoichiometries $Au(CH_3CS_2)$, $Au(PhCS_2)$, and $Au(PhCS_2)(Ph_2CCS_2)$. The X-ray structures of the dithioacetic acid derivative and the mixed-ligand compound have been determined. $Au(CH_3CS_2)$ crystallizes in the triclinic space group $P\bar{1}$ (Z = 2). Lattice constants: a = 12.087 (4), b = 9.698 (3), c = 8.862 (3) Å; α = 95.50 (2), β = 110.57 (2), γ = 92.65 (2)°. Least-squares refinement of 1949 observed reflections has led to a final R factor of 0.045. The structure consists of discrete tetranuclear units, $Au_4(CH_3CS_2)_4$. In the tetrameric molecule the four gold atoms are at the vertices of a rhomb. All the four ligands are bridging and are alternately above and below the plane of the metal cluster. The four equivalent Au–Au distances average 3.013 Å. The mean Au–S bond length is 2.296 Å. If one considers only the S ligands, the geometry of the gold coordination is approximately linear, the mean SAuS angle being 167.7°. $Au(PhCS_2)(Ph_2CCS_2)$ crystallizes in the triclinic space group $P\bar{1}$ (Z = 2). Lattice constants: a = 18.094 (4), b = 11.371 (4), c = 4.912 (3) Å; α = 87.40 (2), β = 98.93 (2), γ = 96.33 (2)°. The final R value was 0.037, for 2326 observations and 120 parameters. The structure is built by monomeric molecules. The gold atom is surrounded by four sulfur atoms, in an approximately planar arrangement. The mean Au–S bond length involving the sulfur atoms of $Ph_2CCS_2^{2-}$, 2.296 (3) Å, is significantly shorter than the corresponding value of 2.369 (3) Å for the $PhCS_2^-$ sulfur atoms. The phenyl ring of the dithiobenzoato ligand is substantially coplanar with the inner chelate rings of the molecule. Vibrational and electronic spectral information for all the compounds is reported and discussed. The Mössbauer spectrum of $Au_4(CH_3CS_2)_4$ is also reported. The isomer shift (relative to the source ^{197}Au in platinum) is 1.40 ± 0.01 mm/s; quadrupole splitting is 6.13 ± 0.02 mm/s. The presence (or absence) of direct Au–Au interactions in $Au_4(CH_3CS_2)_4$ is critically discussed on the basis of the structural and Mössbauer results.

Introduction

Multinuclear d^{10} systems with relatively short intermetallic separations have been the subject of much recent interest.[1] A basic question under study is the presence of attractive interactions between the metal centers (with formally closed shells).[2–4] So far, attention has been mainly focused on Cu(I) cluster compounds. The problem of bonding in these molecules has been studied by means of extended Hückel[2] and SCCC[3] molecular orbital calculations. An interesting structural view of the stability of such clusters has also been presented.[5] The conclusions of these studies do not agree completely.

Unlike copper(I) (which forms clusters with two to eight metal atoms),[2] gold(I) appears to form relatively few multinuclear compounds.[1b,6] Among those that are best documented, and have intermetallic distances short enough to suggest direct Au–Au interaction, there are the 1,1-dithiolato derivatives.[7–9] All reported

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structures of such compounds involve bridged dinuclear molecules Au_2L_2 (L = $(n\text{-}C_3H_7)_2NCS_2^-$,[10] $(i\text{-}C_4H_9)_2NCS_2^-$,[11-13] and $(i\text{-}C_3H_7O)_2PS_2^-$)[14] in which two linearly coordinated metal atoms are components of an eight-membered ring. Mutual interaction of the gold atoms in these compounds is suggested by the relatively short Au–Au contacts, 2.76–3.04 Å (the corresponding value in metallic gold is 2.884 Å[15]), and other structural features, e.g. intermetallic separations are 0.3–0.4 Å less than the S–S ligand bites.

No information is available in the literature on dithio aromatic or dithio aliphatic acid derivatives of gold. One reason why gold(I) dithiocarboxylates are of potential interest is the apparent greater ability of the dithiocarboxylato ligands,[16,17] as compared with the dithiocarbamato or dithiophosphato ligands, of promoting the p–d interactions that are behind the stacking of four-coordinate square-planar d^8 complexes. It has been proposed that interactions of similar nature (mixing of suitable higher empty levels into the repelling d^{10} shells) can lead to an attraction between the d^{10} metal centers.[2,4]

Here, we report the syntheses of the dithioacetic and dithiobenzoic acid derivatives of gold(I), the X-ray structure of the former compound, and vibrational, visible–UV, and Mössbauer spectral information.

Due to the considerable interest that has been devoted to square-planar d^8 complexes with sulfur ligands,[7,18-20] we have also synthesized the mixed-ligand Au(III) derivative $Au(PhCS_2)(Ph_2CCS_2)$ and investigated its X-ray structure and electronic properties.

A preliminary report of the X-ray structure of the gold(I) dithioacetic acid derivative has appeared.[21]

Experimental Section

Dithioacetic acid[22,23] (hereafter dtaH), dithiobenzoic acid[24] (dtbH), and 1,1-diphenyl-2,2-ethylenedithiol[25,26] ($dedH_2$) and their sodium salts were prepared according to known procedures.

Preparation of Complexes. $Au_4(dta)_4$. This red compound was prepared by heterogeneous reaction of $NaAuCl_4{\cdot}2H_2O$ (1 g, 2.5 mmol) with dtaH (1 g, 10.9 mmol) in diethyl ether (50 mL). After the mixture stood for ca. 20 h at room temperature, it was filtered. The solid was recrystallized from carbon disulfide: yield ca. 30%, based on original gold; mp 190–191 °C dec. Anal. Calcd for $C_2H_3S_2Au$: C, 8.34; H, 1.05; S, 22.25; Au, 68.36. Found: C, 8.45; H, 1.10; S, 21.95; Au, 69.40.

Au(dtb). A solution of dtbNa (0.9 g, 5 mmol) in diethyl ether (100 mL) was added, at room temperature, to a solution of 1 g (2.5 mmol) of $HAuCl_4{\cdot}nH_2O$ (49% Au) in 50 mL of the same solvent. The resultant solution was magnetically stirred until a brown-red solid began to separate. After ca. 12 h of standing at room temperature, the reaction mixture was filtered. The solid was washed with diethyl ether and then with water, in order to free the solid from sodium chloride. The residual brown red microcrystalline material was dried under vacuum: yield 0.78 g (89%); mp 273–275 °C. Anal. Calcd for $C_7H_5S_2Au$: C, 24.02; H, 1.44; S, 18.28; Au, 56.26. Found: C, 24.15; H, 1.34; S, 18.46; Au, 56.18.

Au(dtb)(ded). A 25-mL portion of a 4×10^{-2} M solution of dtbH in diethyl ether was added to a solution of $dedH_2$ (0.24 g, 1.0 mmol) in the same solvent (15 mL). To the resultant solution was added, at room temperature, $NaAuCl_4{\cdot}2H_2O$ (0.4 g, 1 mmol) dissolved in methanol (20 mL). The solution became turbid almost immediately. After ca. 12 h of standing at room temperature, a brown solid was filtered and dried under vacuum. The solid was then dissolved in carbon disulfide. A small amount of an insoluble material was filtered off. Upon evaporation of the solution at room temperature, brown needles separated, which were filtered and dried under vacuum. The yield was found to vary from preparation to preparation but in no case was larger than 20%; mp >350 °C. Anal. Calcd for $C_{21}H_{15}S_4Au$: C, 42.56; H, 2.56; S, 21.64; Au, 33.24. Found: C, 42.80; H, 2.48; S, 20.99; Au, 33.85.

Chemical Analyses. These were performed by Mikroanalytisches Laboratorium, Elbach, West Germany.

Infrared Spectra. Infrared spectra were recorded, in the region 5000–250 cm^{-1}, with a Perkin-Elmer 521 spectrophotometer.

Visible–UV Spectra. These were recorded on a Cary 17 spectrophotometer.

Mössbauer Spectra. Mössbauer spectra were supplied by Prof. J. J. Steggerda, Catholic, University, of Nijmegen, Mijmegen, The Netherlands. The apparatus and techniques used to collect the data have been described elsewhere.[27]

X-ray Data and Structure Solution. Au(dtb)(ded). A red, prismatic crystal of $C_{21}H_{15}S_4Au$, with dimensions 0.5 × 0.1 × 0.1 mm was mounted on a Philips PW 1100 four-circle diffractometer equipped with graphite-monochromatized Mo Kα radiation. The crystals belong to the triclinic crystal system, space group $P\bar{1}$. Lattice constants: a = 18.094 (4), b = 11.371 (45), c = 4.912 (3) Å; α = 87.40 (2), β = 98.93 (2), γ = 96.33 (2)° (from the setting angles of 25 centering reflections). The calculated density, assuming 2 molecules per unit cell, is 1.982 g cm^{-3}. The absorption coefficient for Mo Kα is μ = 80.1 cm^{-1}. The intensity data ($\pm h,\pm k,l$) were collected, at room temperature, in the range $2 \leq \theta \leq 25°$ by the $\omega/2\theta$ technique. The scan speed was 0.06° s^{-1} and the scan width 1.2° in θ. Three monitoring reflections were measured every 180 min and did not reveal significant variations in intensity. A total of 3493 reflections were collected, 1167 of which, having $I \leq 3\sigma(I)$, were considered as "unobserved" and excluded from the refinement. The intensity data were corrected for the usual geometrical factors and for absorption, with the method of North et al.[28a] based on the variation in intensity during the azimuthal scan of some reflections. The transmission factors were in the range 0.48–0.99.

The structure was solved by the Patterson method and refined by the full-matrix least-squares program of the SHELX-76[29] package. During the refinement, difference Fourier maps showed that the two phenyl rings of the ded^{2-} ligand are "disordered", having two different orientations with respect to the sulfur–gold plane. The two orientations are about equally represented in the crystal. This disorder was, therefore, treated considering the two orientations together, each with an occupancy factor of 0.5. The phenyl rings were constrained to perfect hexagons (C–C bond distance 1.395 Å). The contribution of the hydrogen atoms at their calculated positions (C–H bond length of 1.08 Å), and with common thermal parameters, was included for the phenyl ring of the dithiobenzoato ligand. Anisotropic thermal parameters for the gold and sulfur atoms were refined. At this stage, a difference Fourier map showed the two biggest maxima of residual density (about 1.8 e/$Å^3$) in the proximity of the gold atom, at a distance of 0.95 Å from it, above and below the sulfur–gold plane. This feature, common to several structures containing heavy atoms, may be due, in our opinion, to the not completely adequate form of the scattering factor curve used in the computations. Anyway, the refinement was stopped since all the shifts in the parameters were less

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Table I. Fractional Atomic Coordinates for Non-Hydrogen Atoms of $Au_4(dta)_4$

atom	*x/a*	*y/b*	*z/c*
Au(1)	0.4902 (1)	0.2903 (1)	−0.0342 (1)
Au(2)	0.4216 (1)	0.4111 (1)	0.2401 (1)
Au(3)	0.3867 (1)	0.1999 (1)	0.4532 (1)
Au(4)	0.4710 (1)	0.0816 (1)	0.1882 (1)
S(1)	0.6863 (5)	0.3659 (7)	0.0966 (8)
S(2)	0.6187 (6)	0.4744 (6)	0.3832 (8)
S(3)	0.5744 (6)	0.2103 (7)	0.6377 (8)
S(4)	0.6646 (6)	0.1153 (6)	0.3682 (8)
S(5)	0.2170 (6)	0.4001 (7)	0.1153 (8)
S(6)	0.1843 (6)	0.1874 (7)	0.3301 (9)
S(7)	0.2818 (6)	0.0108 (7)	0.0114 (8)
S(8)	0.3001 (6)	0.2256 (7)	−0.2076 (7)
C(1)	0.7101 (20)	0.4356 (24)	0.2795 (27)
C(2)	0.8430 (24)	0.4840 (29)	0.3873 (33)
C(3)	0.6804 (20)	0.1762 (24)	0.5551 (27)
C(4)	0.8048 (24)	0.1961 (29)	0.6783 (32)
C(5)	0.1418 (21)	0.2949 (25)	0.1912 (28)
C(6)	0.0061 (27)	0.2936 (31)	0.1048 (34)
C(7)	0.2331 (20)	0.0996 (24)	−0.1483 (27)
C(8)	0.1088 (24)	0.0568 (29)	−0.2623 (33)

Table II. Main Interatomic Distances (Å) in $Au_4(dta)_4$

Au(1)-Au(2)	2.989 (1)	C(1)-S(1)	1.616 (23)
Au(1)-Au(4)	3.013 (1)	C(1)-S(2)	1.700 (20)
Au(2)-Au(3)	3.026 (1)	C(1)-C(2)	1.499 (35)
Au(3)-Au(4)	3.024 (1)	C(3)-S(3)	1.714 (21)
Au(1)-S(1)	2.290 (7)	C(3)-S(4)	1.646 (22)
Au(1)-S(8)	2.288 (7)	C(3)-C(4)	1.506 (34)
Au(2)-S(2)	2.292 (7)	C(5)-S(5)	1.672 (25)
Au(2)-S(5)	2.320 (7)	C(5)-S(6)	1.648 (22)
Au(3)-S(3)	2.294 (6)	C(5)-C(6)	1.547 (36)
Au(3)-S(6)	2.274 (7)	C(7)-S(7)	1.669 (22)
Au(4)-S(4)	2.309 (7)	C(7)-S(8)	1.659 (24)
Au(4)-S(7)	2.300 (7)	C(7)-C(8)	1.499 (35)

than 10% of the standard deviations. The final R value was 0.037, for 2326 observations and 120 parameters. The quantity minimized was $\sum w(\Delta F)^2$, with weighting factors $w = 1/(\sigma^2(F_o) + 0.006F_o^2)$; the weighted R_w, defined as $\sum w^{1/2}\Delta F/\sum w^{1/2}F$, was 0.041. An isotropic extinction parameter[29] was included in the computations: its value refined to 1.40×10^{-5}.

$Au_4(dta)_4$. For the refinement of $Au_4(dta)_4$, a new set of intensity data was collected from a thin red crystal with dimensions 0.69 × 0.15 × 0.02 mm. The crystals belong to the triclinic crystal system, space group $P\bar{1}$ ($Z = 2$). Cell dimensions: a = 12.087 (4), b = 9.698 (3), c = 8.862 (3) Å; α = 95.50 (2), β = 110.57 (2), γ = 92.65 (2)°. The density is 3.966 g cm^{-3}; the absorption coefficient for Mo Kα is μ = 320.2 cm^{-1}. A total of 4601 reflections ($\pm h,\pm k,\pm l$) were measured, in the range $2 \le \theta \le 20°$, by the ω-scan technique. The scan speed was 0.06° s^{-1} and the scan width 2.4°. The intensities were merged to give 2503 independent data, 558 of which, having $I \le 3\sigma(I)$, were considered as unobserved and excluded from the refinement. The intensity data were corrected for the geometrical factors. The severe absorption effects were corrected with the methods of North et al.[28a] and Walker and Stuart;[28b] the transmission factors were in the range 0.99–0.15. The structure was refined by the full-matrix least-squares program of the SHELX-76[29] package, starting from the coordinates of ref 21. The final R value was 0.045 (R_w = 0.046; $w = 1/(\sigma^2(F_o) + 0.0002F_o^2)$). A Fourier difference map again revealed a series of small maxima around each gold atom, at a distance of 0.8–1.0 Å and lying at the vertices of an octahedron centered by the metal. This feature can probably be ascribed to the approximate absorption correction. The atomic scattering factors were taken from ref 30 for Au and from ref 29 for S, C, and H. A correction for anomalous dispersion was applied.

Results

Two gold(I) compounds of stoichiometry Au(dta) and Au(dtb) have been obtained. Their synthesis from gold(III) starting materials indicates stabilization of the metal +1 oxidation state by the dithiocarboxylato ligands. The use of the dinegative ded^{2-} ligand afforded the isolation of the mixed-ligand gold(III) derivative Au(dtb)(ded). The three compounds are air stable. Au(dta) and Au(dtb)(ded) are practically insoluble in polar solvents such as water or ethanol and are slightly soluble in nonpolar or weakly polar organic solvents. Au(dtb) is practically insoluble in any solvent.

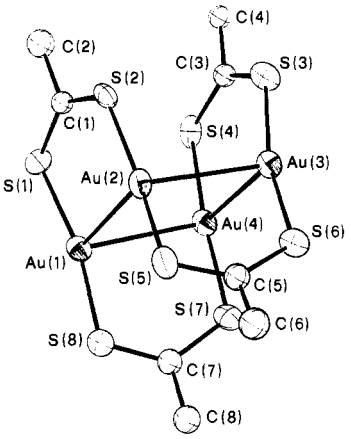

Figure 1. Molecular structure of $Au_4(dta)_4$. Hydrogen atoms have been omitted for clarity.

Table III. Main Interatomic Angles (deg) in $Au_4(dta)_4$

Au(2)-Au(1)-Au(4)	66.6 (1)	Au(1)-S(1)-C(1)	110.8 (9)
Au(2)-Au(1)-S(1)	93.2 (2)	Au(1)-S(8)-C(7)	113.4 (8)
Au(2)-Au(1)-S(8)	95.3 (1)	Au(2)-S(2)-C(1)	114.6 (9)
Au(4)-Au(1)-S(1)	98.2 (2)	Au(2)-S(5)-C(5)	114.7 (8)
Au(4)-Au(1)-S(8)	91.3 (2)	Au(3)-S(3)-C(3)	114.4 (8)
S(8)-Au(1)-S(1)	169.2 (2)	Au(3)-S(6)-C(5)	112.2 (9)
Au(1)-Au(2)-Au(3)	113.9 (1)	Au(4)-S(4)-C(3)	115.0 (8)
Au(1)-Au(2)-S(2)	88.3 (2)	Au(4)-S(7)-C(7)	114.9 (9)
Au(1)-Au(2)-S(5)	100.9 (2)	C(2)-C(1)-S(1)	116.2 (15)
Au(3)-Au(2)-S(2)	97.3 (2)	C(2)-C(1)-S(2)	110.8 (16)
Au(3)-Au(2)-S(5)	88.1 (1)	C(4)-C(3)-S(3)	113.2 (17)
S(2)-Au(2)-S(5)	166.6 (2)	C(4)-C(3)-S(4)	117.0 (16)
Au(2)-Au(3)-Au(4)	66.0 (1)	C(6)-C(5)-S(5)	112.3 (17)
Au(2)-Au(3)-S(3)	99.9 (2)	C(6)-C(5)-S(6)	115.0 (19)
Au(2)-Au(3)-S(6)	92.1 (2)	C(8)-C(7)-S(7)	115.4 (19)
Au(4)-Au(3)-S(3)	90.3 (1)	C(8)-C(7)-S(8)	113.3 (17)
Au(4)-Au(3)-S(6)	104.1 (2)	S(1)-C(1)-S(2)	133.0 (15)
S(3)-Au(3)-S(6)	164.1 (2)	S(3)-C(3)-S(4)	129.6 (15)
Au(1)-Au(4)-Au(3)	113.3 (1)	S(5)-C(5)-S(6)	132.6 (15)
Au(1)-Au(4)-S(4)	97.6 (2)	S(7)-C(7)-S(8)	131.2 (16)
Au(1)-Au(4)-S(7)	89.1 (2)		
Au(3)-Au(4)-S(4)	89.8 (2)		
Au(3)-Au(4)-S(7)	93.3 (2)		
S(4)-Au(4)-S(7)	170.8 (2)		

The detailed geometries of the dithioacetic acid derivative of gold(I) and of the mixed-ligand compound Au(dtb)(ded) were investigated with X-ray methods. The many attempts to obtain single crystals of Au(dtb), in any considerable size, failed completely.

Structures. $Au_4(dta)_4$. Structural information about the compound is reported in Figure 1 and Tables I–III. The crystal structure consists of discrete tetranuclear units $Au_4(dta)_4$. In the molecule the four gold atoms are the vertices of a rhomb. The maximum deviation from planarity is 0.04 Å. The four bridging ligands are alternatively above and below the plane of the metal cluster. Each chelate fragment Au_2S_2CC is substantially planar. The whole molecule has approximate D_2 symmetry. The four equivalent Au–Au distances average 3.013 Å. The unique Au(2)–Au(4) distance is 3.296 (1) Å. The eight Au–S bonds have lengths in the range 2.274–2.320 Å (mean 2.296 Å). These distances to sulfur are unexceptional and may be compared with those in $[(n\text{-}C_3H_7)_2NCS_2Au]_2$, 2.28 (2) Å,[10] and $\{[(i\text{-}C_3H_7O)_2PS_2Au]_2\}_n$, 2.28 (3) Å.[14] The SAuAu angles are in the range 88–101° and average 93.7°. The mean SAuS angle is 167.7° (between ca. 164 and 171°). Thus, if one considers only the sulfur ligands, the geometry of the gold coordination is approximately linear. The deviation from linearity in the S–Au–S coordination is determined by a dihedral angle of about 16°

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table IV. Fractional Atomic Coordinates for Non-Hydrogen Atoms of Au(dtb)(ded)[a]

atom	x/a	y/b	z/c
Au	0.08521 (2)	0.27491 (3)	0.05228 (8)
S(1)	0.1698 (2)	0.1731 (2)	−0.1185 (6)
S(2)	0.1706 (1)	0.4187 (2)	−0.0959 (6)
S(3)	−0.0003 (1)	0.3757 (2)	0.2500 (6)
S(4)	−0.0010 (1)	0.1278 (2)	0.2206 (6)
C(1)	0.2244 (5)	0.3078 (8)	−0.1754 (17)
C(2)	0.2935 (5)	0.3229 (7)	−0.2469 (16)
C(3)	0.3381 (5)	0.2129 (7)	−0.2836 (15)
C(4)	0.4162 (5)	0.2362 (7)	−0.2362 (15)
C(5)	0.4612 (5)	0.1445 (7)	−0.2410 (15)
C(6)	0.4280 (5)	0.0295 (7)	−0.2932 (15)
C(7)	0.3499 (5)	0.0062 (7)	−0.3406 (15)
C(8)	0.3049 (5)	0.0979 (7)	−0.3358 (15)
C(3)′	0.3321 (4)	0.2216 (6)	−0.2789 (14)
C(4)′	0.3495 (4)	0.1967 (6)	−0.5356 (14)
C(5)′	0.3841 (4)	0.0953 (6)	−0.5665 (14)
C(6)′	0.4012 (4)	0.0189 (6)	−0.3407 (14)
C(7)′	0.3837 (4)	0.0438 (6)	−0.0840 (14)
C(8)′	0.3492 (4)	0.1452 (6)	−0.0531 (14)
C(9)′	0.3434 (5)	0.4490 (7)	−0.2704 (15)
C(10)′	0.4216 (5)	0.4518 (7)	−0.2204 (15)
C(11)′	0.4664 (5)	0.5589 (7)	−0.2395 (15)
C(12)′	0.4330 (5)	0.6633 (7)	−0.3086 (15)
C(13)′	0.3548 (5)	0.6605 (7)	−0.3586 (15)
C(14)′	0.3100 (5)	0.5533 (7)	−0.3394 (15)
C(9)	0.3274 (5)	0.4360 (6)	−0.2832 (14)
C(10)	0.3525 (5)	0.4726 (6)	−0.5310 (14)
C(11)	0.3883 (5)	0.5865 (6)	−0.5605 (14)
C(12)	0.3989 (5)	0.6639 (6)	−0.3422 (14)
C(13)	0.3737 (5)	0.6274 (6)	−0.0944 (14)
C(14)	0.3380 (5)	0.5134 (6)	−0.0649 (14)
C(15)	−0.0413 (5)	0.2395 (7)	0.3341 (15)
C(16)	−0.1037 (3)	0.2225 (5)	0.4899 (11)
C(17)	−0.1344 (3)	0.1077 (5)	0.5468 (11)
C(18)	−0.1932 (3)	0.0895 (5)	0.7025 (11)
C(19)	−0.2212 (3)	0.1861 (5)	0.8013 (11)
C(20)	−0.1904 (3)	0.3009 (5)	0.7444 (11)
C(21)	−0.1317 (3)	0.3191 (5)	0.5887 (11)

[a] Primed atoms belong to phenyl rings in alternative orientation. Atoms from C(3) to C(14) have an occupancy factor of 0.5.

Table V. Relevant Bond Distances (Å) in Au(dtb)(ded)

Au-S(1)	2.295 (3)	S(4)-C(15)	1.688 (9)
Au-S(2)	2.296 (3)	C(1)-C(2)	1.342 (13)
Au-S(3)	2.369 (2)	C(2)-C(3)	1.591 (11)
Au-S(4)	2.369 (3)	C(2)-C(3)′	1.437 (11)
S(1)-C(1)	1.765 (9)	C(2)-C(9)′	1.618 (11)
S(2)-C(1)	1.767 (9)	C(2)-C(9)	1.379 (11)
S(3)-C(15)	1.703 (8)	C(15)-C(16)	1.451 (10)

between the planes of the ligands on opposite sides of the metal cluster. The dimensions of the dithioacetato ligands are essentially the same as those observed for dimeric $Pt_2(dta)_4$[31] and $Pd_2(dta)_4$[16] (containing bridging ligands only) but differ from those found in monomeric $Pd(dta)_2$[16] and dtaK[32] in having a longer C–C bond distance (1.51 (3) Å against 1.47 (2) Å in $Pd(dta)_2$ and 1.40 (5) Å in dtaK), a larger SCS angle of 132 (1)° (112.1 (10) and 123.5 (6)°), and a larger angle at sulfur (113.8 (9)° against 87.15 (7)° in the monomeric palladium complex). Upon consideration of the covalent radii of gold (1.33 Å), platinum (1.30 Å), and palladium (1.28 Å), the M–S bond strengths in these compounds appear to be in the order Au–S (2.296 Å) > Pt–S (2.317 Å) > Pd–S (2.327 Å). A theoretical justification of the structural trends above has been proposed;[17] it will not be repeated here.

Au(dtb)(ded). The molecular geometry and labeling scheme for this compound are shown in Figure 2. The fractional atomic coordinates are listed in Table IV. Bond distances and angles

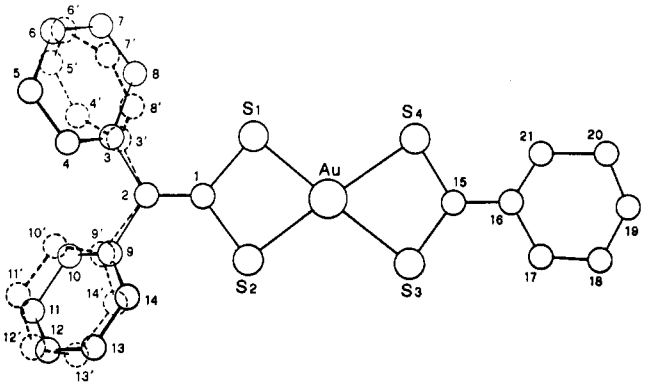

Figure 2. Molecular structure of Au(dtb)(ded). Hydrogen atoms have been omitted for clarity.

Table VI. Bond Angles (deg) in Au(dtb)(ded)

S(1)-Au-S(2)	75.1 (1)	C(1)-C(2)-C(3)	121.4 (8)
S(1)-Au-S(3)	177.2 (1)	C(1)-C(2)-C(3)′	119.9 (8)
S(1)-Au-S(4)	105.4 (1)	C(1)-C(2)-C(9)′	125.1 (8)
S(2)-Au-S(3)	106.2 (1)	C(1)-C(2)-C(9)	119.3 (8)
S(2)-Au-S(4)	178.1 (1)	C(3)-C(2)-C(9)	119.3 (8)
S(3)-Au-S(4)	73.3 (1)	C(3)′-C(2)-C(9)′	114.6 (7)
C(1)-S(1)-Au	89.9 (3)	C(15)-S(3)-Au	86.7 (3)
C(1)-S(2)-Au	89.8 (3)	C(15)-S(4)-Au	87.0 (3)
S(1)-C(1)-S(2)	104.8 (5)	S(3)-C(15)-S(4)	112.9 (5)
S(1)-C(1)-C(2)	127.6 (7)	S(3)-C(15)-C(16)	123.0 (6)
S(2)-C(1)-C(2)	127.4 (7)	S(4)-C(15)-C(16)	124.1 (6)

are given in Tables V and VI, respectively. The gold atom is surrounded by four sulfur atoms in an approximately planar arrangement, as usually happens for gold(III) complexes with sulfur ligands.[1b,6] The maximum deviation from planarity is 0.03 Å. The Au–S(ded^{2-}) bond length, 2.296 (3) Å, is significantly shorter than the Au–S(dtb^-) bond length, 2.369 (3) Å. These values may be compared with those pertaining to the Au–S(MNT^{2-}) and Au–S(n-Bu_2Dtc^-) bonds, 2.293 (13) and 2.326 (5) Å, respectively, in the structure of the mixed-ligand complex Au(n-Bu_2Dtc)(MNT).[33]

The length of the C–S bonds in the ded^{2-} fragment, 1.766 (9) Å, is longer than that in dtb^-, 1.696 (9) Å. The differences in Au–S and C–S bond distances between the halves of the molecule are in fair agreement with the proposal, first made by Jørgensen,[34] that, in square-planar low-spin d^8 complexes, as the C–S bond order increases, the availability of lone pairs on the sulfur atoms decreases and the S → M π bonding decreases in importance.

The C–CS_2 bond length in ded^{2-} has a typical double-bond value of 1.342 (13) Å. The dtb^- phenyl ring is substantially coplanar with the best coordination plane (the angle is 5.8° only); however, the C–C bond distance joining the phenyl ring and its respective chelate ring, 1.451 (10) Å, is not significantly shorter than the accepted single bond between two sp^2-hybridized carbons. This indicates that the π structure of the phenyl ring of dtb^- is of only minor importance in consideration of the bonding in the complex.

Vibrational Spectra. The vibrational spectrum of $Au_4(dta)_4$ is fully consistent with the multinuclear, completely bridged structure revealed by the X-ray work. Only two C–S stretching frequencies are observed ($\bar{\nu}_{as}$(CSS) = 1160 cm^{-1}, $\bar{\nu}_s$(CSS) = 899 cm^{-1}), and these are almost superimposable on those of $Pd_2(dta)_4$[16] and $Pt_2(dta)_4$[31] that also involve only bridging ligands. Different frequencies are shown by the terminal ligands of monomeric $Pd(dta)_2$.[16] The bands due to the aliphatic substituent have similar energies to those of the dithioacetic acid derivatives of other transition metals with different oxidation states and molecular geometries.[16,31,35-37] Also the spectrum of Au(dtb) can be com-

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Table VII. Electronic Spectra of the Gold Dithiocarboxylato Derivatives[a]

compd	medium	transition
Au(dtb)	Nujol	14.0,[b] 18.2,[b] 19.7, 21.8, 25.8, 28.6, *c*
$Au_4(dta)_4$	Nujol	23.1,[b] 26.0,[b] *c*
	CS_2	23.3,[b] 25.6,[b] *c*
Au(dtb)(ded)	Nujol	16.5, 25.0,[b] *c*
	CH_2Cl_2	16.8 (3.54), 25.0,[b] 28.8 (4.92), 35.7,[b] *c*

[a] Energies in 10^3 cm^{-1} (log E_{mol} in parentheses). [b] Intense shoulder. [c] Not measured beyond this frequency.

pletely assigned following previous lines of discussion.[35,38] Relevant frequencies are $\bar{\nu}$(Ph–C) = 1224 cm^{-1}, $\bar{\nu}_{as}$(CSS) = 1039 cm^{-1}, $\bar{\nu}_s$(CSS) = 911 cm^{-1}, and δ(CSS) = 656 cm^{-1}. These frequencies are typical of completely chelated dithiobenzoato complexes. That dithio aromatic and dithio aliphatic complexes with the same metal ion exhibit carbon–sulfur stretching modes at considerably different energies and with markedly different energy separations has been noted previously for other carboxylato complexes.[35]

The spectrum of the mixed-ligand compound Au(dtb)(ded) shows bands that are almost superimposable on those of Au(dtb) and additional bands that are attributable to the ded^{2-} ligand. A band of medium intensity at 1553 cm^{-1} that has no counterpart in the spectrum of Au(dtb) can be reasonably assigned to the ded^{2-} C=CS_2 group.[39] This assignment is in agreement with the X-ray data that show a typical carbon–carbon double-bond length of 1.342 Å. Bands assignable to the $\bar{\nu}$(Ph–C) mode are observed at 1275, 1264, and 1235 cm^{-1}. In the carbon–sulfur region there are bands at 1039, 979, 945, 929, 870, and 804 cm^{-1}. This complicated behavior is not unexpected in light of the differences in SCS angles and C–S bond lengths between the halves of the molecule. No reliable assignments could be made for the M–S modes for any of the compounds.

Electronic Spectra. Electronic spectral information about the present compounds is reported in Table VII. All the bands in the spectra of the three species are characterized by a high intensity. We tentatively suggest that the lowest energy transition for each of the complexes (Au(dtb)(ded), ca. 17 000 cm^{-1}; Au(dtb), ca. 14 000 cm^{-1}; $Au_4(dta)_4$, ca. 23 000 cm^{-1}) be assigned as a M → L* charge transfer and that, in the case of Au(dtb)(ded), this transition mainly involve the excited states of dtb^-. This assignment is in keeping with the position of the intense lowest energy band in $Pt(dtb)_2$, 15 300 cm^{-1} (log E_{mol} = 3.04).[40] A shift to lower energy on going from Au(dtb)(ded) to Au(dtb) through $Pt(dtb)_2$, i.e., on decreasing the oxidation number of the central ion, is characteristic of M → L* charge-transfer transitions.[41] An M → L* transition to ded^{2-}, in the case of the gold(III) compound, would be reasonably expected to occur at relatively higher energies than observed, due to the presumably more antibonding character of the lowest energy π empty levels of ded^{2-} relative to the dtb^- case.[42] Finally, a lower M → L* transition for Au(dtb) than for $Au_4(dta)_4$ is consistent with the higher energy of the lowest empty MO in dta^- than in dtb^-, as shown, for example, by the energies of the first n → π* transition in dtb^-, 20 800 cm^{-1}, and dta^-, 22 400 cm^{-1}.[43]

Mössbauer Spectra. The experimental data points for $Au_4(dta)_4$, at 4.2 K, together with the results of a computer fit for two lines are shown in Figure 3. The isomer shift (relative to the source ^{197}Au in platinum) is 1.40 ± 0.01 mm/s; the quadrupole splitting is 6.13 ± 0.02 mm/s; line widths are 2.11 and 2.27 mm/s; and intensities are 1.1 and 0.87.

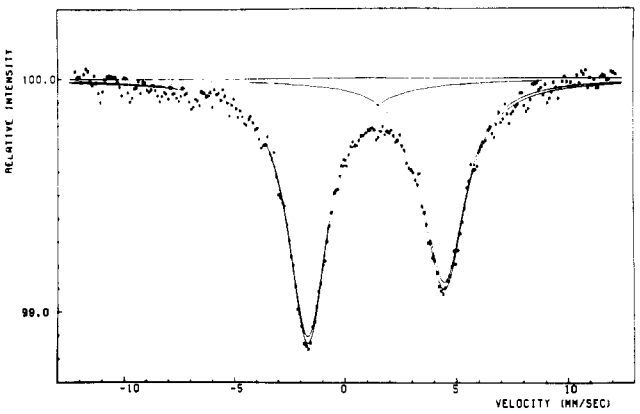

Figure 3. Mössbauer spectrum of $Au_4(dta)_4$.

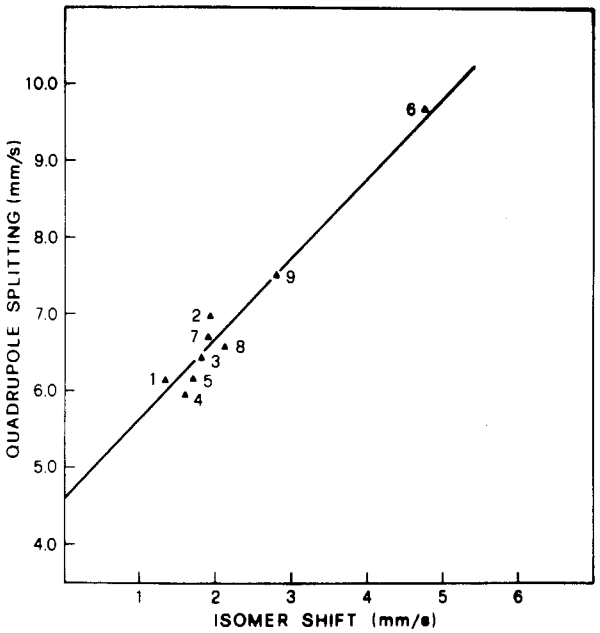

Figure 4. Mössbauer data for some mononuclear and multinuclear, linearly coordinated Au(I) compounds and the values for the peripheral atoms of some gold clusters: 1, $Au_4(dta)_4$; 2, $[Au(S_2O_3)_2]Na_3$;[53] 3, $[Au(n\text{-}C_3H_7)_2NCS_2]_2$;[57] 4, $[Au(i\text{-}C_4H_9)_2NCS_2]_2$;[52] 5, $AuCl_2^-$;[49] 6, $Au(PMePh_2)_2$;[49] 7, $Au_8(PPh_3)_8^{2+}$;[58] 8, $Au_9(PPh_3)_8^{3+}$;[58] 9, $Au(Etu)_2^+$;[49]. The full line represents the correlation between quadrupole splitting and isomer shift proposed by Viegers[52] for linearly coordinated gold(I) compounds.

Discussion

The result of major interest in this study is the attainment of the tetranuclear $Au_4(dta)_4$ compound. With one exception, all structurally determined multinuclear gold(I) compounds in which intermetallic distances are short enough to suggest M–M interaction involve either dinuclear units or monomeric linear molecules forming polymeric gold chains or layers.[1b,6] The exception is[44] the unstable, colorless chloro(piperidine)gold(I). Here, the unbridged, linearly coordinated gold atoms form a loose square cluster with an Au–Au mean distance of 3.301 Å. The rhomboidal geometry of the Au_4 units in $Au_4(dta)_4$ seems to be mainly attributable to steric factors. Interligand S–S and methyl–methyl repulsion would be severe with two alternate pairs of eclipsed ligands and interplanar separations of about 3 Å. On the other hand, there seems little to account for the deviations from linearity in the gold–sulfur coordination except some residual mutual repulsion of the ligands.

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A relevant question for discussion is whether Au–Au bonding interactions contribute to the unique structure of $Au_4(dta)_4$. The Au–Au mean distance of 3.013 Å in this compound, when compared with those in the metal, 2.884 Å,[15] and in the periphery of unbridged cluster compounds such as $[Au_6(PPh_3)_6]^{2+}$, 3.02 Å,[45] and $Au_{11}I_3[P(p\text{-}C_6H_4F)_3]_7$, 2.98 Å[46] (recent MO calculations[47] indicate an important peripheral bonding in these clusters), would seem to suggest attractive Au–Au interactions, possibly as a result of the ability of the dithioacetato ligand system to encourage d–s orbital mixing on gold and to dissipate antibonding density from the plane of the cluster through its delocalized π virtual orbitals.[21]

The Mössbauer results for the tetramer, however, do not provide evidence in support of this view. It has been found[48–53] that an almost linear correlation exists between the isomer shift and quadrupole splitting parameters pertaining to mononuclear, linearly coordinated gold(I) compounds. Figure 4 shows that the values obtained for $Au_4(dta)_4$ appear to follow the same isomer shift/quadrupole splitting relation. Therefore, the Mössbauer results do not give any indication of the presence of direct interactions between the gold atoms of the tetramer. On the other hand, Figure 4 shows that the same conclusion holds for, e.g., the gold atoms in $[Au(i\text{-}C_4H_9)_2NCS_2]_2$ (with an Au–Au distance of 2.76 Å, shorter than that in metallic gold, and for which a bond order of ca. 0.25 has been estimated by Raman spectroscopy[13,54]) or the gold atoms in the periphery of gold clusters like $Au_8(PPh_3)_8^{2+}$ (with peripheral Au–Au distances in the range 2.826 (8)–2.960 (8) Å.[55] The fact that gold atoms can come rather close without showing any interaction in the Mössbauer spectrum might introduce some doubt on the capability of the technique in detecting minor bonding effects. It may be significant, in this respect, that the photoelectron spectra of $AuMe(PMe_3)$ have revealed (in agreement with Xα calculations) a significant Au 5d character in the Au–P bond,[56] a feature that is not evident from the Mössbauer parameters pertaining to a variety of phosphine complexes of gold(I).[49] The involvement of the Au 5d orbitals in bonding is, of course, a prerequisite to any attractive Au(I)–Au(I) interaction.

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Registry No. $Au_4(dta)_4$, 74165-53-0; Au(dtb), 93923-04-7; Au(dtb)(ded), 93923-05-8; $NaAuCl_4$, 15189-51-2; $HAuCl_4$, 16903-35-8; Au, 7440-57-5.

Supplementary Material Available: Listings of hydrogen atom coordinates, thermal parameters, and observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Ditungsten(II) Tetracarboxylates[1]

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Synthetic procedures affording yellow $W_2(O_2C\text{-}t\text{-}Bu)_4$ and $W_2(O_2CMe)_4$ in good yields are described. The pivalate dimer was prepared by reduction of $[WCl_4]_x$ in THF with sodium amalgam in the presence of $NaO_2C\text{-}t\text{-}Bu$. An analogous reaction with sodium acetate failed to provide $W_2(O_2CMe)_4$. The latter was prepared by metathesis of $W_2(O_2CCF_3)_4$ with tetrabutylammonium acetate in toluene. Both of the alkanecarboxylate dimers are extremely air sensitive, especially in solution. They have been characterized by IR, Raman, and mass spectroscopy. An axial triphenylphosphine adduct of the pivalate dimer, $W_2(O_2C\text{-}t\text{-}Bu)_4\cdot 2PPh_3$, has been characterized by low-temperature (−160 °C) X-ray crystallography: monoclinic space group $C2/c$, a = 27.537 (12) Å, b = 9.543 (4) Å, c = 29.131 (14) Å, β = 133.93 (1)°, Z = 4. The structure refined to residuals of R_F = 5.89% and R_{wF} = 4.42%. The molecule resides on an inversion center, and the W–W distance is 2.218 (1) Å. The electrochemical properties of $W_2(O_2C\text{-}t\text{-}Bu)_4$ and $W_2(O_2CMe)_4$ have been investigated by cyclic voltammetry in CH_3CN solution and are compared to those of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ and $Mo_2(O_2C\text{-}n\text{-}Pr)_4$. Paramagnetic, gray $[W_2(O_2C\text{-}t\text{-}Bu)_4]I$ has been obtained from the reaction of the pivalate dimer with I_2 in benzene solution and characterized by IR and ESR spectroscopy. The visible absorption spectra of $W_2(O_2CCF_3)_4$ and $W_2(O_2C\text{-}t\text{-}Bu)_4$ (THF solution) have been studied and are compared to the spectra of the molybdenum analogues and $MoW(O_2C\text{-}t\text{-}Bu)_4$.

Introduction

The molybdenum(II) carboxylates, $Mo_2(O_2CR)_4$, are the most important compounds containing molybdenum–molybdenum quadruple bonds. First reported in the early 1960s by Wilkinson and co-workers,[3] they remain the key starting materials in Mo_2^{4+} chemistry and have been the objects of numerous physical and theoretical studies.[4] The most commonly used method of preparation is the thermal reaction of $Mo(CO)_6$ with a carboxylic acid, either neat or, preferably, in an inert solvent such as diglyme or

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