Synthesis and Low-frequency Vibrational Spectra of Some Bis(alkanethiolato)- and Bis(benzenethiolato)-aurate(I) Complexes

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Salts containing bis(alkanethiolato)aurate(I) ions, $[Au(SR)_2]^-$ (R = Me or Bu^t), or bis(benzenethiolato)aurate(I) ions, $[Au(SPh)_2]^-$, have been prepared from the corresponding dihalogenoaurate(I) salts by displacement of halide by thiolate ion. No evidence is found for the formation of multinuclear thiolate-bridged complexes of the type previously postulated for the gold(I)–thiomalate system. The observation of single ν(Au–S) bands in the far-i.r. spectra of the $[Au(SR)_2]^-$ (R = Me or Bu^t) salts is consistent with the presence of mononuclear anions in which gold(I) exhibits its usual linear two-co-ordination.

COMPOUNDS with gold–sulphur bonds are of considerable interest because of their pharmacological properties.[1,2] A recent ^{13}C n.m.r. study of the reaction of thiomalic acid with disodium thiomalatogold, $Na_2[Au\{SCHCO_2(CH_2CO_2)\}]$, gave evidence that clusters $[Au_4(SR)_7]^{3-}$ (RS^- = disodium thiomalate) are formed in solution and that further addition of thiomalate does not result in the formation of $[Au(SR)_2]^-$.[3] This behaviour is similar to that of the other univalent Group 1B metals copper(I) and silver(I), for which multinuclear complexes of the type $[M_4(SR)_6]^{2-}$, $[M_5(SR)_7]^{2-}$, and $[M_5(SR)_6]^-$ (RS^- = alkane- or arene-monothiolate) have been prepared as crystalline salts,[4-7] but no corresponding salts of mononuclear ions such as $[M(SR)_2]^-$ have been prepared, except for R = C_6F_5, a strongly electron-withdrawing group.[8] The postulated structure of the $[Au_4(SR)_7]^{3-}$ ion involves three- and four-co-ordinate gold(I).[3] In the majority of its complexes, gold(I) is two-co-ordinate. Some examples of three- and four-co-ordination have been reported for gold(I),[9-15] but the factors which lead to the adoption of the higher co-ordination numbers are not yet understood. The present work was undertaken in order to find out what types of anionic complexes are formed by gold(I) with simple alkane- or arene-monothiolate ligands, and to provide further data concerning the co-ordination number of gold(I).

An additional aim was to study the vibrational spectra of the compounds prepared and to assign the gold–sulphur stretching vibrations. Very little information about such vibrations has been reported in the literature to date.

EXPERIMENTAL

Preparation of Compounds.—All preparations were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques.[16]

Thiols. Commercial methanethiol (Matheson), 2-methylpropane-2-thiol (1,1-dimethylethanethiol) (RDH, Prosynth), benzenethiol (BDH, LR) and tetrachloroauric(III) acid (BDH, LR) were used without further purification. Tetraphenylphosphonium bromide,[17] bis(triphenylphosphine)iminium chloride,[18] and the tetra-alkylammonium dihalogenoaurates(I) [19] were prepared by literature methods. The tetraphenylphosphonium and bis(triphenylphosphine)iminium dihalogenoaurates(I) were prepared by metathesis from the corresponding halides and tetra-alkylammonium dihalogenoaurates(I).

Tetrabutylammonium bis(methanethiolato)aurate(I), $[NBu_4][Au(SMe)_2]$. Methanethiol (0.5 g, 10.4 mmol) was condensed onto a frozen mixture of sodium hydroxide solution (2.4 cm^3 of 1 mol l^{-1}; contains 2.4 mmol Na[OH]) and ethanol (10 cm^3). Tetrabutylammonium dichloroaurate(I) (0.6 g, 1.2 mmol) was then added and the mixture was warmed to room temperature, stirred, and filtered. On addition of water (14 cm^3) a heavy oil separated from the filtrate. The mixture was extracted with chloroform and the chloroform extract was filtered and evaporated under vacuum to produce an oil which crystallized when the last of the chloroform was removed. The product was purified by redissolving in chloroform and adding dry diethyl ether to give white crystals, m.p. 86—88 °C (Found: C, 40.5; H, 7.5; N, 2.7. $C_{18}H_{42}AuNS_2$ requires C, 40.5; H, 7.9; N, 2.6%).

Bis(triphenylphosphine)iminium bis(methanethiolato)aurate(I), $[N(PPh_3)_2][Au(SMe)_2]$. Methanethiol (0.5 g, 10.4 mmol) was condensed onto a frozen mixture of sodium hydroxide solution (1.5 cm^3 of 1 mol l^{-1}; contains 1.5 mmol Na[OH]) and ethanol (10 cm^3). Bis(triphenylphosphine)iminium dichloroaurate(I) (0.6 g, 0.7 mmol) was added and the mixture was warmed to room temperature and stirred to produce a clear solution. Water (4.5 cm^3) was added and the solution allowed to stand overnight to produce white crystals, m.p. 188—190 °C (decomp.) (Found: C, 55.0; H, 4.4; N, 1.7. $C_{38}H_{36}AuNP_2S_2$ requires C, 54.9; H, 4.5; N, 1.5%).

Tetrabutylammonium bis(2-methylpropane-2-thiolato)aurate(I), $[NBu_4][Au(SBu^t)_2]$. 2-Methylpropane-2-thiol (0.4 g, 4.4 mmol) and $[NBu_4][AuCl_2]$ (0.6 g, 1.2 mmol) were added to a mixture of sodium hydroxide (2.4 cm^3 of 1 mol l^{-1}; contains 2.4 mmol Na[OH]) and ethanol (10 cm^3) and the mixture was stirred to produce an almost clear solution. After filtration and addition of water (10 cm^3) to the filtrate, the product separated as an oil on standing in the refrigerator overnight. The oil was extracted with chloroform and the chloroform extract was evaporated under vacuum to produce an oil which was dried over molecular sieves. The product was not analysed, but its far-i.r. spectrum shows that it contains the $[Au(SBu^t)_2]^-$ ion (see Results and Discussion).

Tetraphenylphosphonium bis(2-methylpropane-2-thiolato)aurate(I), $[PPh_4][Au(SBu^t)_2]$. 2-Methylpropane-2-thiol (0.22 g, 2.4 mmol) and tetraphenylphosphonium dibromoaurate(I) (0.5 g, 0.8 mmol) were added to a solution of potassium hydroxide (0.09 g, 1.6 mmol) in ethanol (2 cm^3). The white precipitate of potassium bromide was filtered off and the ethanol evaporated under vacuum to give an oil which quickly solidified. The product was purified by recrystallization from acetone to give yellow crystals, m.p. 163—170 °C (Found: C, 54.1; H, 5.3; P, 4.4. $C_{32}H_{38}AuPS_2$ requires C, 53.8; H, 5.4; P, 4.3%).

Bis(triphenylphosphine)iminium bis(2-methylpropane-2-thiolato)aurate(I), $[N(PPh_3)_2][Au(SBu^t)_2]$. 2-Methylpropane-2-thiol (0.32 g, 3.5 mmol) and $[N(PPh_3)_2][AuCl_2]$ (0.7 g, 0.9 mmol) were added to a mixture of sodium hydroxide solution (1.75 cm^3 of 1 mol l^{-1}; contains 1.75 mmol Na[OH]) and ethanol (20 cm^3) and the mixture stirred. Water (1 cm^3) was added and the solution was filtered. Water (20 cm^3) was added to the filtrate and crystals of the product separated from the solution on standing in the refrigerator overnight, m.p. 168—170 °C (Found: C, 58.1; H, 5.4; N, 1.5. $C_{44}H_{48}AuNP_2S_2$ requires C, 57.8; H, 5.3; N, 1.5%).

Tetraphenylphosphonium bis(benzenethiolato)aurate(I), $[PPh_4][Au(SPh)_2]$. Benzenethiol (0.27 g, 2.5 mmol) and $[PPh_4][AuBr_2]$ (0.5 g, 0.8 mmol) were added to a solution of potassium hydroxide (0.09 g, 1.6 mmol) in ethanol (2 cm^3). After stirring, the solution was filtered and the collected solid was treated with chloroform. Evaporation of the resulting chloroform solution gave a white solid which was recrystallized from chloroform–acetone, m.p. 162—163 °C (Found: C, 57.5; H, 4.2; P, 4.2. $C_{36}H_{20}AuPS_2$ requires C, 57.3; H, 4.0; P, 4.1%).

Bis(triphenylphosphine)iminium bis(benzenethiolato)-aurate(I), $[N(PPh_3)_2][Au(SPh)_2]$. Benzenethiol (1.07 g, 9.7 mmol) and $[N(PPh_3)_2][AuCl_2]$ (0.6 g, 0.7 mmol) were added to a mixture of sodium hydroxide solution (1.5 cm^3 of 1 mol l^{-1}; contains 1.5 mmol Na[OH]) and ethanol (10 cm^3). The solution was stirred and dimethylformamide (10 cm^3) was added to dissolve the remaining solids. The resulting solution was filtered and water (4.5 cm^3) was added to the filtrate. The product separated as white crystals on standing, m.p. 158—159 °C (Found: C, 60.3; H, 4.3; N, 1.3. $C_{48}H_{40}AuNP_2S_2$ requires C, 60.4; H, 4.2; N, 1.5%).

2-*Methylpropane-2-thiolatogold*(I), $[Au(SBu^t)]$. Tetrachloroauric(III) acid (0.09 g, 0.25 mmol) was dissolved in ethyl acetate (5 cm^3) and 2-methylpropane-2-thiol (0.08 g, 0.9 mmol) was added to the resulting solution. The solution turned deep red and a precipitate slowly formed. The mixture was warmed to 50 °C for 0.5 h whereupon the product separated as a light orange precipitate (Found: C, 17.4; H, 3.5. C_4H_9AuS requires C, 16.8; H, 3.2%).

Benzenethiolatogold(I), $[Au(SPh)]$. Tetrachloroauric(III) acid (0.09 g, 0.25 mmol) was dissolved in ethyl acetate (5 cm^3) and benzenethiol (0.1 g, 1.0 mmol) was added to the resulting solution. The solution was stirred and the pale yellow product separated over a period of 0.5 h (Found: C, 24.3; H, 1.9. C_6H_5AuS requires C, 23.5; H, 1.7%).

Microanalyses.—Microanalyses were carried out by Professor A. D. Campbell at the University of Otago, Dunedin.

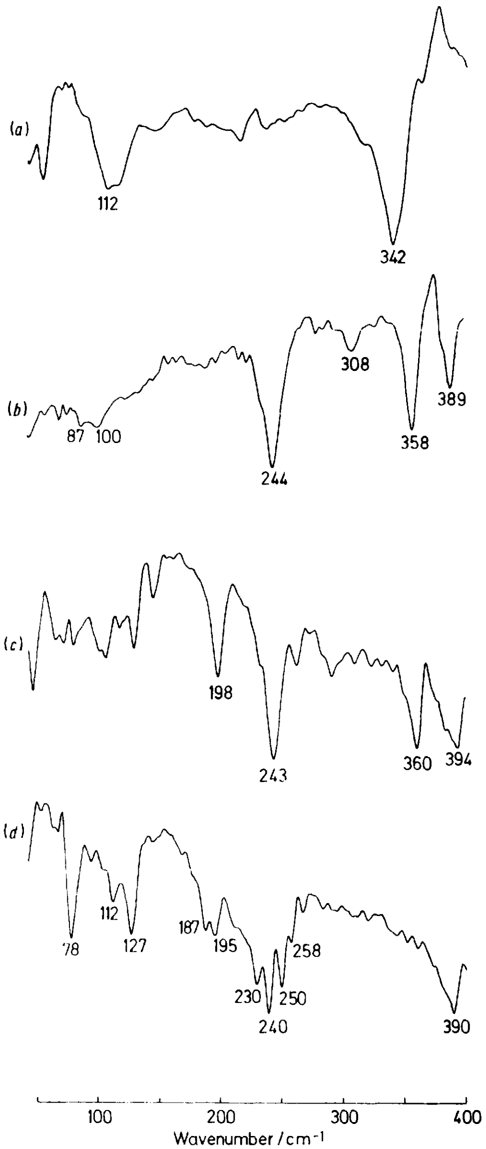
Spectroscopy.—Infrared spectra in the range 400—4 000 cm^{-1} were obtained on a Perkin-Elmer 397 spectrometer. Spectra were run on Nujol mulls between KBr plates, and were calibrated by using the spectrum of polystyrene. The far-i.r. spectra (50—400 cm^{-1}) were obtained on a Grubb-Parsons Cube Mk II interferometer fitted with a 6.25-μm Mylar-film beam splitter. Spectra in this range were run on petroleum jelly mulls between Polythene plates, and were calibrated by using the spectrum of water vapour. Spectra at *ca*. 125 K were recorded in the Grubb-Parsons GRM 01 low-temperature cell cooled with liquid nitrogen.

Raman spectra were obtained on a Jasco R300 Raman spectrometer and were excited with a Control 540 argon-ion laser (488.0 nm line). The spectra were run on polycrystalline solids in glass capillary tubes at room temperature (*ca*. 293 K) and were calibrated by means of the argon-ion plasma lines.

RESULTS AND DISCUSSION

The only anionic complexes obtained as crystalline salts were the bis(thiolato)aurate(I) complexes $[Au(SR)_2]^-$ (R = Me, Bu^t, or Ph). These were prepared from the corresponding dihalogenoaurate(I) salts by halide–thiolate metathesis (see Experimental section). When tetra-alkylammonium cations were used as counter ions the products were usually difficult to crystallize, or were liquids at room temperature. It was therefore found more convenient to use tetraphenylphosphonium (PPh_4^+) or bis(triphenylphosphine)iminium $N(PPh_3)_2^+$ as counter ions, although the vibrational spectra of the resulting compounds were more difficult to analyse (see below). Solid complexes containing multinuclear anions of the type $[Au_x(SR)_y]^{x-y}$ were not obtained under the preparative conditions used. This does not prove that such complexes cannot be prepared, but it is significant that studies of the corresponding copper(I) and silver(I) systems produced only multinuclear complexes $[M_x(SR)_y]^{x-y}$ with a $y : x$ ratio less than 2 : 1, even when the solutions from which these complexes crystallized contained up to a four-fold excess of thiolate ion relative to metal ion,[4-7] whereas in the present work it was possible to recrystallize salts of the $[Au(SR)_2]^-$ complexes in the absence of excess of thiolate ion. Thus, in contrast to the findings for the gold(I)–thiomalate system,[3] $[Au(SR)_2]^-$ complexes can be readily prepared with simple alkane- and arene-monothiolates. The existence of such complexes is entirely in accord with the observed predominance of two-co-ordination for gold(I) complexes.

The far-i.r. spectra of $[NBu_4][Au(SMe)_2]$, $[NBu_4][Au(SBu^t)_2]$, and $[PPh_4][Au(SBu^t)_2]$ are shown in the Figure. The higher-wavenumber spectra of all of the compounds studied could be satisfactorily assigned to internal vibrations of the thiolate groups, or to cation vibrations. The remaining bands are expected to arise from external modes. The expected structure of the $[Au(SR)_2]^-$ ions would involve a linear S–Au–S group, although a variety of point-group symmetries is possible depending on the disposition of the alkyl or aryl groups. (Assuming a non-linear C–S–Au linkage, some of the possible point groups for a rigid structure are C_{2h}, C_{2v}, or C_2.) Some idea of the expected vibrational modes and their frequencies can be obtained by reference to the vibrational spectra of the isoelectronic mercury(II) thiolates, $[Hg(SR)_2]$. In the solid state $[Hg(SMe)_2]$ has linear S–Hg–S co-ordination with additional weak intermolecular Hg $\cdots$ S interactions,[20] and an i.r. band at 337 cm^{-1} has been assigned to the asymmetric stretching mode ν_{asym}(Hg–S) of the S–Hg–S group.[21] The far-i.r. spectrum of $[NBu_4][Au(SMe)_2]$ is very simple (Figure) and there is little doubt that the very strong band at 342 cm^{-1} can be assigned to ν_{asym}(Au–S) of the linear S–Au–S group in the anion. No strong Raman band was found which might be assigned to the symmetric stretching mode ν_{sym}(Au–S). However, the Raman spectrum was not of good quality; the only definite band below 800 cm^{-1} was a weak one assigned to ν(C–S) at 712 cm^{-1}. The far-i.r. spectrum also shows a medium-intensity band at 112 cm^{-1}. By analogy with the results for $[AuCl_2]^-$, for which ν_{asym}(Au–Cl) occurs at 330 cm^{-1} and δ(Cl–Au–Cl) at 116 cm^{-1},[19,22] this band can be assigned to the δ(S–Au–S) mode.



Far-i.r. spectra (at *ca.* 120 K) of (*a*) $[NBu_4][Au(SMe)_2]$, (*b*) $[NBu_4][Au(SBu^t)_2]$, (*c*) $[PPh_4][Au(SBu^t)_2]$, and (*d*) $[PPh_4][Au(SPh)_2]$

The far-i.r. spectrum of $[NBu_4][Au(SBu^t)_2]$ (Figure) contains bands in the 300—400 cm^{-1} region which can be assigned to internal vibrations of the thiolate ligand.[21,23] This leaves a strong band at 244 cm^{-1} which can be assigned to ν_{asym}(Au–S). Comparison with the value for the corresponding mercury compound is not as straightforward in this case, since solid $Hg(SBu^t)_2$ is an infinite polymer in which the mercury atoms are bridged by thiolate groups, resulting in a co-ordination number of four for mercury.[24] The reported values for the i.r.-active ν_{asym}(Hg–S) modes are 172 [solid $Hg(SBu^t)_2$],[21] 246 (solution in pyridine),[25] and 274 cm^{-1} (solution in CCl_4).[25] In spite of the strong dependence of this frequency on the physical state of the sample, it is clear that the observed values support the above ν_{asym}(Au–S) assignment for $[Au(SBu^t)_2]^-$. Also, it can be noted that the ratio of the ν_{asym}(Au–S) wavenumbers for $[Au(SMe)_2]^-$ and $[Au(SBu^t)_2]^-$ (1.40 : 1) is nearly the same as the ratio of the square roots of the masses of the thiolate ligands (1.38 : 1), as would be expected if the structure and bonding in these ions are similar. The Raman spectrum of this compound was not of very good quality, but it showed a band assigned to ν(C–S) at 590 cm^{-1} and a weaker band at 230 cm^{-1}, tentatively assigned to the symmetric stretching mode ν_{sym}(Au–S). The far-i.r. spectrum of $[PPh_4][Au(SBu^t)_2]$ (Figure) shows a strong band assigned to ν_{asym}(Au–S) at 243 cm^{-1}. Thus, as was found in the case of the dihalogenoaurates(I),[19,22] the anion vibrational frequencies are almost independent of the counter ion, as would be expected for solids containing non-interacting anions.

By analogy with other Group 1B thiolates, the ν(M–S) vibrations of benzenethiolate complexes are expected to occur at about the same frequency as those for the corresponding 2-methylpropane-2-thiolate compounds.[7]

Bands (cm^{-1}) assigned to ν(C–S), ν(Au–S), and δ(S–Au–S) vibrations

Compound	ν(C–S) Raman	ν(Au–S) i.r.	δ(S–Au–S) i.r.
$[NBu_4][Au(SMe)_2]$	712	342	112
$[N(PPh_3)_2][Au(SMe)_2]$	695	344	
$[NBu_4][Au(SBu^t)_2]$	590	244	100, 87
$[PPh_4][Au(SBu^t)_2]$		243	
$[N(PPh_3)_2][Au(SBu^t)_2]$	586	246	
$[Au(SBu^t)]$		244	
$[Au(SPh)]$		219, 191	

A group of bands in the range 230—260 cm^{-1} is observed in the far-i.r. spectra of $[PPh_4][Au(SPh)_2]$ (Figure) and of $[N(PPh_3)_2][Au(SPh)_2]$. The reason for the multiplicity of the ν(AuS) bands in these cases is not obvious. The Raman spectrum of $[PPh_4][Au(SPh)_2]$ in this region shows a single strong band at 257 cm^{-1}. Thus, the vibrational data are insufficient to allow a definite conclusion concerning the structure of the anion in this complex to be reached at this time.

The far-i.r. spectra of $[Au(SBu^t)]$ and $[Au(SPh)]$ were also examined. For $[Au(SBu^t)]$ a single band occurs at 244 cm^{-1}, which is exactly the same frequency as ν_{asym}(Au–S) in the $[Au(SBu^t)_2]^-$ salts (see above). The occurrence of a single ν(Au–S) band in [Au(SBu^t)] parallels the situation previously found for [Ag(SBu^t)] [ν(Ag–S) at 240 cm^{-1}], but contrasts with that for [Cu(SBu^t)] where three bands are observed [ν(Cu–S) at 158, 200, and 231 cm^{-1}].[7] In the case of [Au(SPh)], two bands occur at 191 and 219 cm^{-1}, slightly lower than those tentatively assigned to ν(Au–S) in the [Au(SPh)$_2$]$^-$ salts.

A summary of the vibrational assignments is given in the Table. It was not possible to assign all of the expected bands in the spectra of salts of the large cations PPh$_4$$^+$ and N(PPh$_3$)$_2$$^+$ because of interference by cation bands.

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REFERENCES

[1] R. J. Puddephatt, 'The Chemistry of Gold,' Elsevier, Amsterdam, 1978.
[2] P. J. Sadler, *Struct. Bonding (Berlin)*, 1976, **29**, 171.
[3] A. A. Isab and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1976, 1051.
[4] I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, 1976, **19**, L41.
[5] I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 1976, 103; *Aust. J. Chem.*, 1978, **31**, 2195.
[6] I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 1976, 68.
[7] G. A. Bowmaker and L.-C. Tan, *Aust. J. Chem.*, 1979, **32**, 1443.
[8] W. Beck, K. H. Stetter, S. Tadros, and K. E. Schwarzhaus, *Chem. Ber.*, 1967, **100**, 3944.
[9] W. Cochran, F. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 1957, 2816.
[10] E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1970, **92**, 4114.
[11] N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805.
[12] G. C. H. Jones, P. G. Jones, A. C. Maddock, M. J. Mays, P. A. Vergnano, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1440.
[13] M. J. Mays and P. A. Vergnano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.
[14] R. V. Parish and J. D. Rush, *Chem. Phys. Lett.*, 1979, **63**, 37.
[15] C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1979, 1730.
[16] D. F. Schriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969, ch. 7.
[17] J. Dodonow and H. Medox, *Ber. Deutsch. Chem. Ges.*, 1928, **61**, 907.
[18] J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, 1974, **15**, 84.
[19] P. Braunstein and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1973, 1845.
[20] D. C. Bradley and N. R. Kunchur, *J. Chem. Phys.*, 1964, **40**, 2258.
[21] A. J. Canty, R. Kishimoto, G. B. Deacon, and G. J. Farquharson, *Inorg. Chim. Acta*, 1976, **20**, 161.
[22] G. A. Bowmaker and R. Whiting, *Aust. J. Chem.*, 1976, **29**, 1407.
[23] R. Gaufris, A. Perez, and J. L. Bribes, *Bull. Soc. Chim. Fr.*, 1971, 2898.
[24] N. R. Kunchur, *Nature (London)*, 1964, **204**, 468.
[25] P. Biscarini, L. Fusina, and G. Nivelini, *J. Chem. Soc., Dalton Trans.*, 1974, 2140.