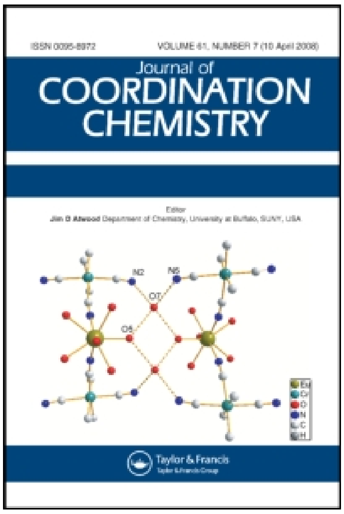


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

GOLD(I) COMPLEXES OF *N*-ALKYL SUBSTITUTED IMIDAZOLIDINE-2-THIONES: SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE

M. Sakhawat Hussain[a]; Anvarhusein A. Isab[a]
[a] Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

To cite this Article Hussain, M. Sakhawat and Isab, Anvarhusein A.(1985) 'GOLD(I) COMPLEXES OF *N*-ALKYL SUBSTITUTED IMIDAZOLIDINE-2-THIONES: SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE', Journal of Coordination Chemistry, 14: 1, 17 — 26

To link to this Article: DOI: 10.1080/00958978508080673

URL: http://dx.doi.org/10.1080/00958978508080673

J. Coord Chem., 1985, Vol. 14, pp. 17-26
0095-8972/85/1401-0017$18.50/0

GOLD(I) COMPLEXES OF *N*-ALKYL SUBSTITUTED IMIDAZOLIDINE-2-THIONES: SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE

M. SAKHAWAT HUSSAIN† and ANVARHUSEIN A. ISAB
Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

(Received April 12, 1984; in final form June 4, 1984)

N-alkyl-substituted imidazolidine-2-thiones act as monodentate ligands coordinating through sulfur. The gold(I) complex, chloro(*N*-propyl-1,3-imidazolidine-2-thione)gold(I), [(PrImt)AuCl] crystallizes in the monoclinic space group *C2/c* with $a = 10.164(4)$, $b = 14.836(2)$, $c = 13.590(9)$A, $\beta = 95.08(5)^\circ$ and $Z = 8$. The X-ray structure determined using intensity data collected on a CAD4 diffractometer and refined by full-matrix least-squares methods, converged to a conventional *R* factor value of 0.077 for 1153 observed reflections. Gold(I) has a linear coordination with an S-Au-Cl angle of 173.3° and Au-S and Au-Cl distances of 2.26(1) and 2.27(1)A. The ^{13}C nmr spectra of the complexes indicated a high-field shift of about 8 ppm for the C–S carbon, suggesting identical coordination sites in the solid and solution states. This large shift in ^{13}C resonance can be used as a diagnostic nmr observation for location of coordination sites in solution of these and other C–S bonded complexes.

INTRODUCTION

Gold compounds have been important in the management of rheumatoid arthritis and inflammatory disorders for several years.[1–3] For example, gold(I) thiolates (AuSR), in which SR is a thiomalate or a substituted thioglucose group, are the most commonly used anti-arthritic gold preparations.[4–6] Most other air-stable, water-soluble gold(I) compounds used in chrysotherapy (gold treatment), are thiol complexes.[7] Despite this importance, no structural analyses have been carried out on the mercapto-gold drugs due to the difficulty in obtaining crystals suitable for diffraction studies. However, circular dichroism, Mössbauer and infra-red spectroscopy were successfully used[8–10] to establish the linear coordination of gold in and the overall structures of a few drugs. We are studying crystalline gold(I) compounds with naturally occuring ligands such as thiones and halides in an effort to understand the likely chemistry of gold drugs. Our rationale for these model systems is based on an implicit assumption of much of the medical literature[7] that "gold" is perhaps the most active moiety in all gold drugs used in medicine. If the ligands were playing any crucial role, the currently marketed gold drugs, such as triethylphosphinegold(I) chloride, Auranofin, Sanochrysin, sodium gold(I) thiomalate (Myocrisin), 3-triethylphosphinogold(I)-2,3,4,6-tetra-*O*-acetyl-1-thio-*β*-*D*-glucopyranoside and gold(I) thioglucose (Solganol), having a wide variety of ligands, are likely to vary in their overall effectiveness, as is the case with their markedly different enzyme inhibition ability.[11]

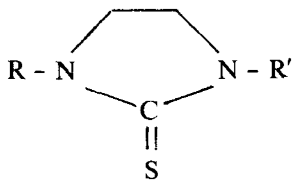
Among several model systems under investigation are the gold(I) complexes of mono-alkylated imidazolidine-2-thione shown below. These ligands generally form crystalline gold(I) complexes which can be studied by spectroscopic and diffraction techniques.

---

†Author to whom correspondence should be addressed.

R = -H; R' = -$CH_2CH_2CH_3$ (Prlmt)

R = -H; R' = -CH_2CH_3 (Etlmt)



The present paper describes the synthesis and spectroscopic studies of gold(I) complexes of Prlmt and Etlmt and the single crystal X-ray structure of chloro(*N*-propyl-1,3-imidazolidine-2-thione)gold(I).

EXPERIMENTAL

Chemicals

All chemicals and deuterated solvents were obtained from Fluka Chemical Company and were used without further purification.

Preparation and Crystal Growth of the Complexes

The ligands Etlmt and Prlmt were prepared by the literature method.[12–13] Gold(I) was generated by passing SO_2 into aqueous solution of chloroauric acid using the procedure described earlier.[14] As soon as the solution became colorless, the ligand was added keeping the gold(I)-to-ligand ratio at 1:1. A white crystaline product was immediately formed. Crystals for diffraction studies were obtained by slow evaporation of methanolic solutions of the complexes. The elemental analyses of the products performed on a Carlo Erba (Italy) Elemental Analyzer are given below.
Calcd. for $C_6H_{12}N_2S$ (Prlmt, m.p. 87°): C, 50.0; H, 8.3; N, 19.4%; Found: C, 51.3; H, 8.5; N, 20.1%. Calcd. for $C_5H_{10}N_2S$ (Etlmt, m.p. 76°): C, 46.2; H, 7.7; N, 21.5%; Found: C, 45.6; H, 7.6; N, 21.5%. Calcd. for $C_6H_{12}N_2SAuCl$ ([PrlmAuCl], m.p. 124°): C, 18.69; H, 3.11; N, 7.26%; Found: C, 18.67; H, 3.10; N, 7.27%. Calcd. for $C_5H_{10}N_2AuCl$ ([EtlmtAuCl], m.p. 142°): C, 16.55; H, 2.76; N, 7.72%; Found: C, 16.12; H, 2.69; N, 7.64%].

Spectroscopic Measurements

The infra-red spectra of all compounds were obtained using a Perkin-Elmer IR 180 or a Beckman Microlab infrared spectrophotometer using KBr pellets. ^1H nmr spectra were obtained at 200 MHz on a Varian XL-200 spectrometer operating in the pulsed Fourier transform mode. ^1H chemical shifts were measured using internal *t*-butyl alcohol and are reported relative to the methyl proton resonance of sodium 2,2-dimethyl-2-silopentane-4-sulfonate (DSS). The methyl resonance of *t*-butyl alcohol was at 1.23 ppm relative to DSS. All ^1H nmr measurements were done using d_4-methanol as a solvent. The ^{13}C nmr spectra were obtained at 50.3 MHz on the same spectrometer using d_6-acetone as solvent and the chemical shifts were measured using 1,4-dioxane as the internal reference with its resonance at 67.4 ppm relative to DSS.

X-Ray Data Collection and Structure Solution

Chloro(*N*-propyl-1,3-imidazolidine-2-thione)gold(I), [(Prlmt)AuCl]. A well formed clear crystal 0.18 × 0.15 × 0.16 mm was mounted on a glass fibre in an arbitrary orientation. Lattice constants were obtained by the least-sqaures refinement of the diffraction geometry of 23 centred reflections having $20.2 < 2\theta < 30.5°$, located by the automatic SEARCH program and measured at an ambient temperature of 23±3°. The crystal data are: $C_6H_{12}N_2SAuCl$, $M = 376.5$, Monoclinic, $a = 10.164(4)$ $b = 14.836(2)$ $c = 13.590(9)$A, $\beta = 95.08(5)^\circ$ $U = 2041.3A^3$, $F(000) = 1392$ $D_m = 2.45$ g cm^{-3}, $Z = 8$, $D_c = 2.45$ g cm^{-3}, Mo-K_α radiation $\lambda = 0.71073$ A, μ (Mo) = 142.6 cm^{-1}. No cell of higher symmetry was found by Delauney reduction with TRACERII.[15] Space group *C2/c* based on systematic absences, *hkl* with $(h+k)$ odd and *h0l* with *l* odd. The density was measured by floating the crystals in a solution containing 1,3-dibromopropane and bromoform. The solution density was determined with a pycnometer. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP8/A computer using graphite-monochromated Mo-K_α radiation and the ZIGZAG method in the ω - 2θ scan mode with a scan range of $(1.20+0.35 \tan\theta)^\circ$ centred about the calculated Mo-K_α peak positions. Background counts were measured for half of the total scan time by extending the scan range 25% on either side of the scan limits. A total of 4051 $h, k, \pm l$ reflections for $2.0 < 2\theta < 50.0^\circ$ including standard and extinct reflections was measured. Three standards, monitored every 8000 s of X-ray exposure time, gave no indication of crystal deterioration. The crystal orientation was checked each 75 reflections. The intensities were corrected for background, Lorentz and polarization effects, and equivalent and duplicate reflections were averaged ($R_{int} = 0.013$) to obtain 1788 unique relections, 1153 of which with $I > 3\sigma$ (I) were used in the analysis.

The coordinates for the Au atom were obtained from Patterson peaks calculated using the SHELX76 package.[16] A difference Fourier map phased on the coordinates of the Au atom led to the location of all non-hydrogen atoms. A few cycles of isotropic refinement were followed by several cycles of anisotropic refinement. The positions of hydrogen atoms were not evident from a difference Fourier map even at the last stages of refinement. In the final cycles, all non-hydrogen atoms were refined anisotropically while the hydrogen atoms were fixed at calculated positions with an isotropic thermal parameter of $U = 0.06$. The last refinement of 136 variables led to the values of $R = 0.077$ and $R_w = 0.079$; the value of w was based on counting statistics and was equal to

TABLE I
Fractional atomic coordinates for the [(PrImt)AuCl] molecule. (The esd's are given in parentheses.)

Atom	*x/a*	*y/b*	*z/c*
Au	0.1565(2)	0.2167(1)	0.2602(1)
S	0.1814(12)	0.0978(8)	0.3632(8)
Cl	0.1553(12)	0.3302(7)	0.1478(7)
N(1)	0.056(3)	0.203(2)	0.490(2)
N(2)	0.131(3)	0.078(2)	0.553(2)
C(1)	0.121(3)	0.129(2)	0.468(2)
C(2)	0.059(4)	0.119(3)	0.631(2)
C(3)	0.015(4)	0.210(3)	0.587(3)
C(4)	0.207(4)	-0.006(3)	0.566(3)
C(5)	0.343(4)	0.014(4)	0.615(4)
C(6)	0.432(5)	-0.066(3)	0.632(4)
HN1	0.0259	0.2619	0.4469
H1C2	-0.0260	0.0781	0.6449
H2C2	0.1219	0.1266	0.6981
H1C3	0.0651	0.2648	0.6275
H2C3	-0.0902	0.2192	0.5862
H1C4	0.1571	0.0520	0.6110
H2C4	0.2162	-0.0362	0.4941
H1C5	0.3314	0.0444	0.6852
H2C5	0.3905	0.0604	0.5682
H1C6	0.5256	-0.0443	0.6667
H2C6	0.4459	-0.0976	0.5618
H3C6	0.3869	-0.1136	0.6787

TABLE II
Results of spectroscopic measurements on *N*-substituted 2-thiones and their Gold(I) complexes.

Measurement	Compound							Ref.
		υ(NH)	υCN+ δNH	Δ(NH)	υ(CS)	Vibration below 450 cm^{-1}		
Infra-red Absorptions[a]	EtImt	3300sh–3200vs	1505vs	610–630s br	515vs	360vw		26
	(EtImt)AuCl	3310vs	1550vs br	565 ms br	490vs	380m, 330vs		
	PrImt	3300sh–3200vs	1410vs br	610–620 s br	515vs	375w		
	(PrImt)AuCl	3305vs	1540vs br	555 ms br	495vs	355m, 330vs		
^{1}H NMR Spectra[b]		δCH_3(a)	δCH_2(b)	δCH_2(c)	δCH_2(d)	δCH_2(e)		
	EtImt	1.146	—	3.575	3.513	3.702		
	(EtImt)AuCl	1.229	—	3.570	3.678	3.892		
	PrImt	0.949	1.638	3.520	3.535	3.711		
	(PrImt)AuCl	0.984	1.708	3.509	3.699	3.897		
^{13}C NMR Spectra[c]		δCH_3(a)	δCH_2(b)	δCH_2(c)	δCH_2(d)	δCH_2(e)	δC (f)	
	EtImt	12.090	—	41.581	41.581	48.171	184.119	
	(EtImt)AuCl	12.142	—	42.663	42.663	49.859	175.672	
	Shifts	-0.052		-1.082	-1.082	-1.688	+8.447	
	PrImt	1.330	20.844	41.780	48.583	48.881	184.469	
	(PrImt)AuCl	11.087	20.811	42.713	49.494	50.618	176.177	
	Shifts	+0.243	+0.033	-0.933	-0.914	-1.737	+8.292	

[a] Solid state spectra using KBr disks: sh=shoulder, br=broad, vs=very sharp, vw=very weak, m=medium, s=sharp. [b] Resonance assignments are shown in Figures 1 and 2. Down- and high-field shifts relative to the free ligands are indicated by negative and positive signs. [c] Solvents are given in the experimental section.

$1.000/(F^2 + 0.0187F^2)$. The largest shift in any parameter in the final refinement cycle was 0.18 times its estimated standard deviation. The highest peak of 1.1 e/A^3 in the final difference Fourier map was in the vicinity of the gold atom.

The full-matrix least-squares refinement was based on F_o, and the function minimized was $\Sigma w[|F_o| - |F_c|]^2$. Agreement factors are defined as $R = \Sigma|F_o|-|F_c|/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. All calculations were carried out on the University of Petroleum and Minerals IBM 3033 computer using SHELX76. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[17], and for H atoms from Stewart, Davidson and Simpson.[18] Anomalous dispersion corrections were taken from Cromer and Liberman.[19] The final atomic coordinates for heavy atoms and calculated positions for the hydrogen atoms are given in Table I. The anisotropic thermal parameters for these atoms and lists of the observed and calculated structure factors are available as supplementary material from the Editor-in-Chief upon request.

RESULTS AND DISCUSSION

Only mono-complexes of general formula [LAuX] were obtained as crystalline products. Solid bis-complexes of the type [L_2AuX] were not obtained under the preparative conditions used even with an excess of the ligands. The inability to obtain 3-coordinated or anionic bis-gold(I) complexes is contrary to the observation that similar unsubstituted imidazoline-2-thione ligands are known to form anionic bis-gold(I) complexes.[20] Similarly, trigonal copper(I) complexes of both mono- and disubstituted ligands are also known.[21-22]

Spectroscopic Studies

The results of the infra-red, ^{1}H and ^{13}C nmr measurement for the ligands and their gold(I) complexes are given in Table II. The complexes are S-bonded to the metal, as indicated by the shift in the υ(C-N) and υ(C-S) bands with respect to the free ligands (Table II). The υ(Au-Cl) and υ(Au-S) bands are expected to fall in the 600-250 cm^{-1} range. By analogy with the spectrum of $AuCl_2$[23-24] for which υ(Au-Cl) occurs at 330 cm^{-1} and δ(Cl-Au-Cl) at 116 cm^{-1}, the peak at 330 cm^{-1} in the present complexes can be assigned to the υ(Au-Cl) mode. Similarly, by comparison with known compounds[25] a strong band at 375 cm^{-1} can be assigned to υ(Au-S). The ligand band at 1510 cm^{-1}, attributed to a mixing of δ(NH) and υ(CN), undergoes an upward shift to 1550-1540vs cm^{-1}. The υ(NH) bands in the complexes shift about 110 cm^{-1} to higher wavenumbers as was observed in chloro-bis(*N*-ethyl-1,3-imidazolidine-2-thione) copper(I)[21] indicating that NH is involved in an intermolecular hydrogen bond with the chloride ion. This was confirmed by the X-ray structure determination: N-H--Cl = 3.289A.

The ^{1}H nmr spectrum of PrImt is shown in Fig. 1. The spectra of the ligands gave no NH resonance due to a fast rate exchange between NH and the solvent. The multiplets for $-CH_3$ and β-CH_2 protons (Fig. 1: a and b protons) of the propyl group were observed in the usual spectral range (Table II). A triplet from α -CH_2 was centred at 3.520 ppm and the ring protons (Fig. 1: d and e protons) in the ligands have two sets of multiplets centred at 3.535 and 3.711 ppm. The triplet from the α-CH_2 protons overlapped the multiplets for the 'a' type protons of the ring in free PrImt whereas the signals for α -CH_2 protons in the complex [(PrImt)AuCl] are clearly resolved into a triplet centred at 3.509 ppm and an AB signal for the ring protons. The ^{13}C nmr spectral data for the ligands and their complexes are given in Fig. 2 and Table II. A significant high-field shift of about 8 ppm with respect to the free ligand was observed for the C-S carbon in the

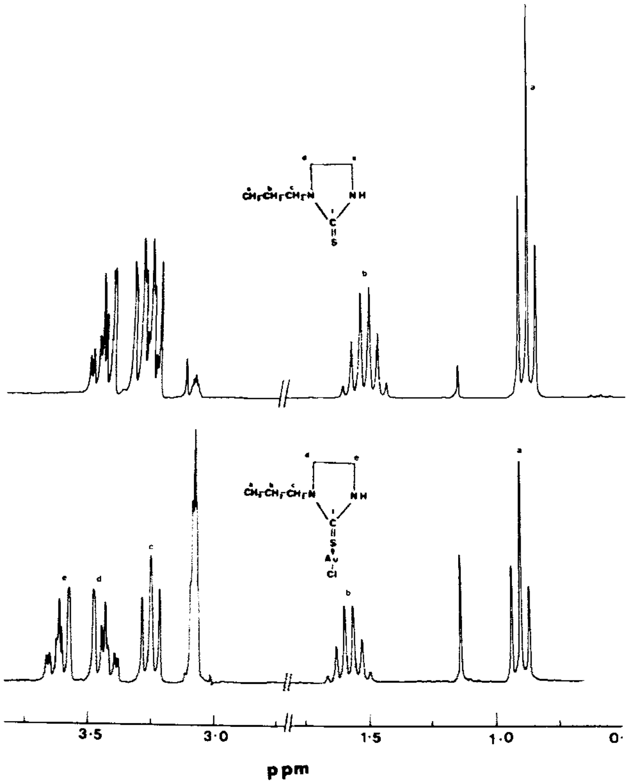


FIGURE 1 ^{1}H-nmr spectrum showing resonance assignments in the free (Prlmt) ligand and its Gold(I) complex. The values for the chemical shifts given in Table II correspond to the centres of multiplets.

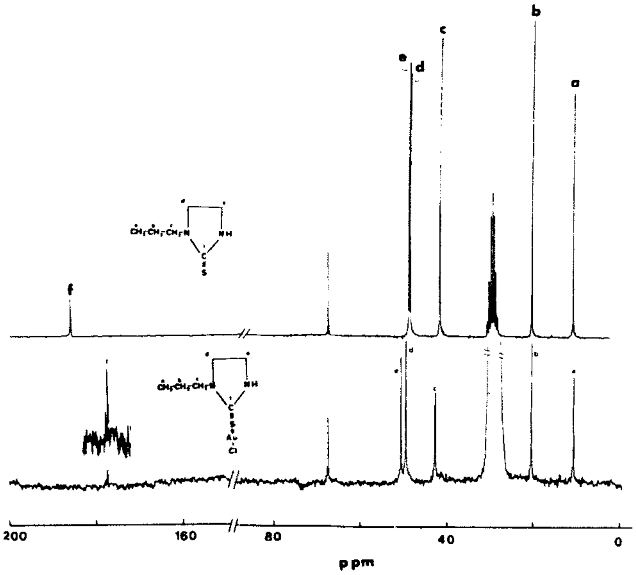


FIGURE 2 ^{13}C nmr spectrum of the free (Prlmt) ligand and the [(Prlmt)AuCl] complex showing resonance assignments. The values of the chemical shifts for different carbon atoms are given in Table II.

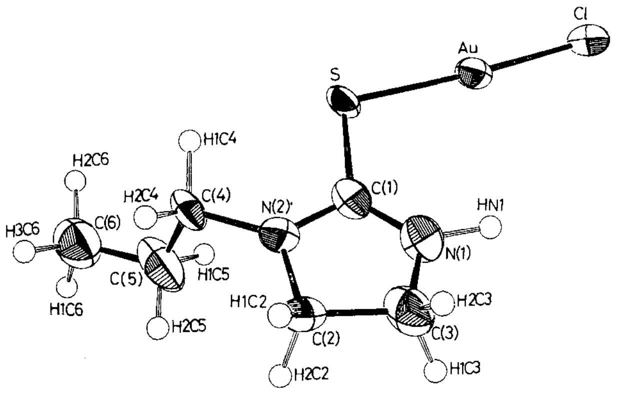


FIGURE 3 Perspective view of the [(Prlmt)AuCl] molecule showing atom labelling as identified in Table I. Hydrogen atoms are shown as spheres at the calculated positions.

complexes. This shift clearly indicates coordination of the ligand to gold(I) through the sulfur atom. It also suggests that the complexes resist dissociation in solution and that the mode of coordination in solution is identical to that in the solid state. The large value of shifts for the C–S carbon observed in ^{13}C spectra of these complexes, in general, can be used as a diagnostic nmr observation for the location of coordination sites of these and other similar gold complexes in solution. As expected, the alkyl groups (ethyl or propyl) have identical effects so far coordination site is concerned.

X-Ray Structure of (Prlmt)AuCl

Figure 3 depicts the molecular geometry about the gold atom and the packing of molecules in the unit cell is illustrated in Figure 4. The structure consists of discrete

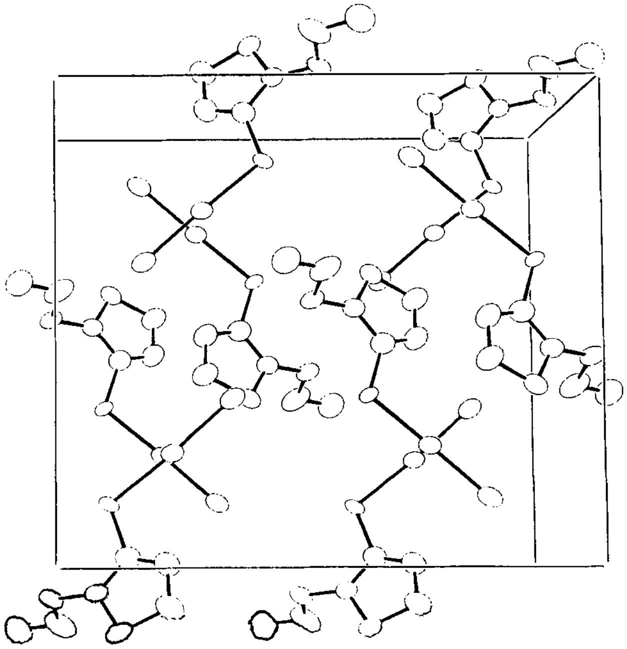


FIGURE 4 A view of the unit cell showing the molecular packing in [(Prlmt)AuCl].

TABLE III
Bond distances and angles for [(Prlmt)AuCl], with estimated standard deviations in parentheses.

(a) Bond distances (A)	
Au-Cl	2.27(1)
Au-S	2.25(1)
C(1)-S	1.67(4)
C(1)-N(1)	1.33(4)
C(1)-N(2)	1.37(4)
N(2)-C(2)	1.47(5)
C(2)-C(3)	1.53(5)
N(1)-C(3)	1.42(4)
N(2)-C(4)	1.47(4)
C(4)-C(5)	1.50(6)
C(5)-C(6)	1.48(5)
(b) Bond angles (deg):	
Cl-Au-S	172.5(4)
Au-S-C(1)	107(1)
S-C(1)-N(1)	131(1)
S-C(1)-N(2)	124(1)
N(1)-C(1)-N(2)	106(2)
C(1)-N(1)-C(3)	117(1)
N(1)-C(3)-C(2)	101(2)
C(3)-C(2)-N(2)	103(2)
C(1)-N(2)-C(4)	112(2)
C(1)-N(2)-C(2)	112(2)
C(2)-N(2)-C(4)	124(2)
N(2)-C(4)-C(5)	110(1)
C(4)-C(5)-C(6)	121(3)
(c) Non-bonded distances and angles:	
Au. . .Au$^{(a)}$	3.168(5)
Au. . .S$^{(a)}$	4.097(9)
S. . .Cl$^{(a)}$	4.851(8)
N(1). .Cl$^{(a)}$	3.31(2)
N(2). .Cl$^{(b)}$	4.65(2)
N(1). .N(2)	2.156(4)

At symmetry positions (a): $-x$, y, $1/2-z$, (b): $1/2-x$, $1/2-y$, $1-z$.

monomeric units of [(Prlmt)AuCl] in which the gold(I) atom exhibits the usual linear coordination. The S-Au-Cl angle is 172.5(3)° (Table III). The deviation of about 8° from strict linearity may be explained on the basis of a weak N(1)-H--Cl hydrogen bonding interaction. The N(1)--Cl distance of 3.31(2)A is of the order of the van der Waals distance (3.30 A) for a hydrogen bond of the type N-H--Cl.[26] Such a hydrogen bonding interaction are also evident from the infra-red spectra of the complexes as mentioned earlier. The Au-Au distance of 3.168(5)A between two independent [(Prlmt)AuCl] molecules is significantly longer than the corresponding distance of 2.884A observed in metallic gold[27] suggesting that any Au-Au interaction is very weak, if at all present, in the present complex. The non-hydrogen atoms of the Prlmt ligand are co-planar with a maximum deviation of 0.023A. The average angle for the regular pentagon is 108(2)°; the average CNC angle of 115° in the five-membered ring is greater than the NCN angle of 106° or the average NCC angle of 102°.

TABLE IV
Some distances (A) and angles (deg) in related Imidazolidine-2-thione complexes[a].

Compound	M-X	M-S	C-S	X(S)-M-S	M-S-C	Ref
(diEtlmt)$_2$CuCl	2.258(2)	2.218(3)	1.702(5)	120.8(1)	108.2(2)	21
(Etlmt)$_2$CuCl	2.333(3)	2.229(3)	1.698(4)	112.9(1)	110.5(3)	22
(Imt)$_2$AuCl.H$_2$O	3.62[b]	2.279(8)	1.718(22)	167.1(2)	110.5(8)	20
(Melmt)$_4$Ni(ClO$_4$)$_2$		2.224(4)	1.713(11)		108.4(5)	34
(Etlmt)HgCl$_2$	2.52(1)	2.50(1)	1.70(3)	108.6(3)	106.5(1)	35
(diMelmt)SbCl$_3$	2.533(1)	2.511(1)	1.743(5)	86.9(1)		36
(Prlmt)AuCl	2.269(8)	2.263(8)	1.67(4)	172.5(4)	107(1)	this work

[a]An average value is listed for more than one distance and angle of the same kind. [b]Non-bonded distance.

Comparison with Related Structures

Some selected bond distances and angles for a few related compounds are listed in Table IV. The linear coordination is consistent with Au(I) coordination in several other known structures. For instance, the Au(I) atom is linearly coordinated to two S atoms in Na$_3$Au(S$_2$O$_3$)$_2\cdot$2H$_2$O[28] and is bis(ethylenethiourea)gold(I) chloride hydrate.[20] Similar linear structures are known for [(Ph$_3$)PAuCl][29], [(PhO)$_3$PAuCl][30] and [Ph$_3$PAu(CN)][31] complexes. EXAFS studies have also indicated linear S-Au-S coordination for disodium(thiomalato-*S*)gold(I) (Myocrysin) and (thioglucopyranosyl-*S*)gold(I) (Solganol), two drugs used for the treatment of rheumatoid arthritis.[32] The Au-S bond lengths of 2.246(8)A in [(Prlmt)AuCl] are slightly shorter than the corresponding distances of 2.279(8)A observed[20] in [(lmt)$_2$AuCl]$\cdot$H$_2$O or of 2.73A derived from EXAFS studies for Myocrysin in Solganol.[32] The Au-Cl distance of 2.267(8)A is similar to that of 2.273(3)A in [(PhO)$_3$PAuCl][30] and 2.279(3)A in [Ph$_3$PAuCl].[29] The C-S distance of 1.67(4)A agrees well with that of 1.673(5)A observed in the free ligand DiMelmt.[33]

ACKNOWLEDGEMENT

The authors gratefully acknowledge support from the Research Committee of the University of Petroleum and Minerals (Grant CY/ORGOMETL/64).

REFERENCES

1. N.L. Gottlieb, *Chrysotherapy, Bull. Rhem. Dis.*, **27**, 912 (1977).
2. R.J. Puddephatt, The Chemistry of Gold (Elsevier, Amsterdam, 1978).
3. D.H. Brown and W.E. Smith, *Chem. Soc. Rev.*, 217 (1980).
4. A. Lorber and T.M. Simon, *Gold Bull.*, **12**, 149 (1979).
5. C.F. Shaw, *Inorg. Perspect. Biol. Med.*, **2**, 287 (1979).
6. R.W. Mason, *Pharmacology*, **15**, 536 (1977).
7. D.T. Walz, M.J. DiMartino and B.M. Sutton, Anti-inflammatory Agents (Academic Press, New York, 1974), p. 217.
8. D.H. Brown, G.C. McKinley and W.E. Smith, *J. Chem. Soc., Dalton Trans.*, 1874 (1977).
9. K. Brown, R.V. Parish and C.A. McAuliffe, *J. Amer. Chem. Soc.*, **103**, 4943 (1981).
10. P.G. Jones, A.G. Maddock, M.J. Mays, M.M. Muir and A.F. Williams, *J. Chem. Soc., Dalton Trans.*, 1434 (1977).
11. D. Burkhardt, R.W. Stephens, P. Ghost and T.K.F. Taylor, *Agents Actions*, **8**, 251 (1978).
12. M. Gilbert, G. Michel, A. Georges and K. Jacky, C.R. *Hebd. Seances Acad. Sci. Ser. B.*, 286 (1978).
13. G.D. Thorn, *Can. J. Chem.*, **33**, 1278 (1955).
14. A.A. Isab and P.J. Sadler, *Biochim. Biophys. Acta*, **492**, 322 (1977).
15. S.L. Lawton, TRACERII-Lattice Transformation-Cell Reduction computer program (Northwestern Version), April 1967.

16. G.M. Sheldrick., SHELX76 Programs for Crystal Structure Determination, University of Gottingen, West Germany.
17. D.T. Cromer and J.B. Mann, *Acta Cryst.* **A24,** 321 (1968).
18. R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys.*, **42,** 3175 (1965).
19. D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53,** 1891 (1970).
20. P.G. Jones, J.J. Guy and G.M. Sheldrick, *Acta Cryst.* **B32,** 82 (1976).
21. L.P. Battaglia, A.B. Corradi, F.A. Devillanova and G. Verani, *Transition Metal Chem.*, **4,** 264 (1979).
22. F.A. Devillanova, G. Verani, L.P. Battaglia and A.B. Corradi, *Transition Metal Chem.*, **5,** 362 (1980).
23. P. Braunstein and R.J.H. Clark, *J. Chem. Soc., Dalton Trans.*, 1845 (1973).
24. G.A. Bowmaker and R. Whiting, *Aust. J. Chem.*, **29,** 1407 (1976).
25. G.A. Bowmaker and B.C. Dobson, *J. Chem. Soc., Dalton Trans.*, 267 (1981).
26. W.C. Hamilton and J.C. Ibers, Hydrogen Bonding in Solids, (W.A. Benjamin, New York, 1969), p. 16.
27. D.N. Batchelder and R.O. Simons, *J. Appl. Phys.*, **36,** 2864 (1965).
28. H. Ruben, A. Zalkin, M.O. Faltens and D.H. Templeton, *Inorg. Chem.*, **13,** 1836 (1974).
29. N.C, Balziger, W.E. Bennett and D.M. Soboroff, *Acta Cryst,* **B/2,** 962 (1976)
30. P.B. Hitchcock and P.L. Pye, *J. Chem. Soc., Dalton Trans.*, 1457 (1977).
31. P.L. Bellon, M. Manassero and M. Sansoni, *Ric. Sci,* **39,** 173 (1969)
32. M.A. Mazid, M.T. Razi, P.J. Sadler, G.N. Greaves, S.J. Gurman, M.H.J. Koch, J.C. Philips, *J. Chem. Soc., Chem. Comm.*, 1261 (1980).
33. C. Chieh and S.K. Cheung, *Can. J. Chem.*, **61,** 211 (1983).
34. M.E. O'Neill, E.S. Raper, I.W. Nomell and J.A. Daniels, *Inorg. Chim. Acta,* **54,** L243 (1981).
35. M. Cannas, F.A. Devillanova, G. Marongiu and G. Verani, *J. Inorg. Nucl. Chem.*, **43,** 2383 (1981).
36. B. Rubin, F.J. Heldrich, W.K. Dean, D.J. Williams and A. Vichbach, *Inorg. Chem.*, **20,** 4434 (1981).
37. P.G. Jones and A.G. Maddock, *J. Chem. Soc., Dalton Trans.*, 1437 (1977).