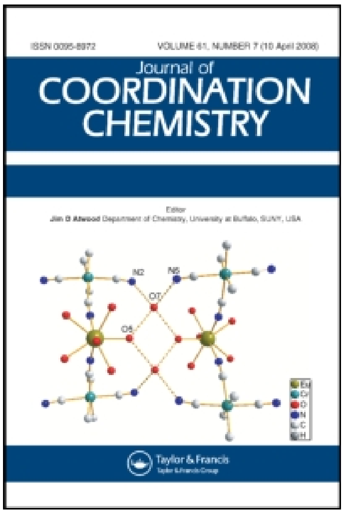

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COMPLEXATION OF IMIDAZOLIDINE-2-THIONE AND ITS DERIVATIVES WITH GOLD(I) CYANIDE

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New 1:1 complexes of the type [LAu-CN] where L = imidazolidine-2-thione and its *N*-alkylated derivatives are obtained from reactions between the thione ligands and gold(I) cyanide. The complexes are characterized by elemental analyses, ^{13}C NMR and IR spectroscopy.

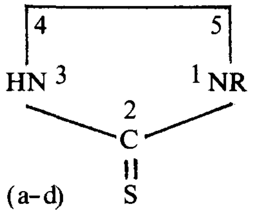
Keywords: Gold, thiones, chrysotherapy, complexes, synthesis

INTRODUCTION

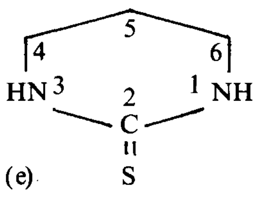
Gold(I) cyanide was the first inorganic compound introduced as a drug for the treatment of tuberculosis. The cyanide group was later replaced by thiols and gold(I) thiolates were used as drugs by Lande,[1] who erroneously assumed a relationship between tuberculosis and arthritis. Gold(I) thiolates such as gold(I) thiomalate (Myocrisin) and gold(I) thioglucose (Solganol) have been used as anti-arthritic drugs since then for rheumatoid arthritis.[2–4]

In this paper, we report the synthesis and ^{13}C NMR and IR spectroscopic studies of new cyanogold(I)-imidazolidine-2-thione complexes and derivatives. Two factors prompted us to report these complexes. First, to our knowledge no complex has been reported which has a thione and a CN$^-$ group as the *trans* ligands for gold(I).[5] Secondly, it has recently been reported that chrysotherapy patients who are tobacco smokers accumulate gold from injectable gold drugs into their red blood cells while non smokers do not.[6] Cyanide from the inhaled smoke alters the metabolism of gold.[7] The results presented here show that gold(I) cyanide forms stable complexes with thiones.

The following complexes are reported



(a–d)



(e)

(a) R = H = Imidazolidine-2-thione (Imt)

(b) R = C_2H_5 = *N*-Ethylimidazolidine-2-thione (EtImt)

(c) R = C_3H_7 = *N*-Propylimidazolidine-2-thione (EtImt)

(d) R = *i*-C_3H_7 = *N*-isopropylimidazolidine-2-thione (PrImt)

(e) 1, 3-Diazinane-2-thione (Diaz)

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RESULTS AND DISCUSSION

Our recent studies[8–11] of the gold(I) complexes of the ligands listed above have revealed that gold(I) forms linear complexes of the types [R-Au-X] and $[R_2Au]X$ where R = imidazolidine-2-thione and its *N*-alkylated derivatives and X = halide. Similarly, linear [R-Au-CN] species are formed by the reaction of Au(I) cyanide with the ligands. The analytical data given in Table I are consistent with the mono-complexes. It has recently been reported[12] that triphenylphosphoniomethanide(CH_2PPh_3) also forms a stable 1:1 complex with gold(I) cyanide. This complex has been characterized using various physical techniques.

TABLE I
Analytical data for the gold(I) complexes†.

Complex	M.Pt (°C)	Colour	H	C	N
[(Imt)AuCN]	199–201°C	White Crystalline	1.78 (1.85)	15.48 (14.76)	12.91 (12.92)
[(EtImt)AuCN]	160–161°C	White Powder	2.62 (2.83)	20.19 (20.40)	11.66 (11.89)
[(PrImt)AuCN]	161–162°C	Brown powder	3.25 (3.26)	23.07 (22.88)	11.58 (11.44)
[(IPrImt)AuCN]	178–179°C	White crystalline	3.05 (3.26)	22.71 (22.88)	11.25 (11.44)
[(Diaz)AuCN]	166–169°C	White crystalline	2.24 (2.36)	18.09 (17.68)	12.34 (12.38)

†The corresponding calculated values are given in parentheses.

Infrared Studies

The results of the IR measurements of the free ligands and their cyanogold(I) complexes are given in Table II. A significant shift of ν(CN) from 2220 cm^{-1} to 2115–2130 cm^{-1} indicates CN bonded to the gold(I). This downward shift of 90–105 cm^{-1} for the CN group clearly indicates an increase in the ionic nature of the cyano ligand.[13] For the $[AuCN(CH_2PPh_3)]$ complex the ν(CN) band was observed at 2142 cm^{-1}, which is somewhat less than in the present thione system. For this complex ν(CN) was shifted by 80 cm^{-1} from Au-CN. A ν(CN) value of 2140 cm^{-1} has been reported for the $O_3S_2AuCN^{2-}$ system.[5]

The strong absorption in the 3200–3300 cm^{-1} region in the free ligands as well as in the complexes indicates that the ligands are in the thione forms and that gold(I) is not bonded *via* an NH group. A shift of 20–25 cm^{-1} in the ν(C=S) band is also indicative of gold(I) bonded *via* a thione group. In the lower IR region, the absorption around 320–340 cm^{-1} is due to the Au-S vibration.[14]

TABLE II

Significant infrared absorptions for the ligands and their gold(I) complexes in the region 4000–200 cm^{-1}.

Compound	ν(N–H)	ν(CN)+δ(NH)	ΔNH	$\nu_{C=S}$	$\nu_{(CN)}$ from [AuCN]	vibrations below 450 cm^{-1}
Imt	3200 sh	1500 sh	680 sh	510 w		
AuCN					2220 sh	
[(Imt)AuCN]	3300–3400 br	1525 sh	660 br	490 w	2115 sh	345 w, 270 w, 240 w
EtImt	3200 br	1504 sh	620 br	515 vs		285 sh
[(EtImt)AuCN]	3200 sh	1545 sh	625 w	490 w	2130 sh	340 w, 270 w, 240 sh
PrImt	3210 br	1520 sh	610 sh	525 sh		
[(PrImt)AuCN]	3200 br	1510 sh	600 w	495 w	2130 sh	320 w, 290 w
IPrImt	3210 br	1520 sh	610 sh	525 sh		
[(IPrImt)AuCN]	3200 br	1510 sh	605 sh	520 w	2130 sh	275 sh, 245 w
Diaz	3200 sh	1560 sh	640 sh	510 w		514 sh, 340 sh
[(Diaz)AuCN]	3300–3200 br	1560 sh	620 sh	515 w	2130 sh	440 w, 410 sh, 370 w, 335 w

Carbon-13 NMR Studies

Figure 1 shows the ^{13}C NMR spectra of free imidazolidine-2-thione and its gold(I)-CN complex in DMSO/acetone solvent. The spectrum of AuCN was not recorded because of its insolubility in this solvent system. The ^{13}CN resonance was observed in the 143-145 ppm region for all of the complexes (Table III), which is a clear indication of the existence of CN in the coordination sphere of the metal atom. For the [Au(CN)CH$_2$PPh$_3$] complex[12] the cyano carbon chemical shift was observed at 153.8 ppm, about 10 ppm higher than for the thione complexes under investigation. There are two factors to account for this difference: the solvents in which the NMR spectra were measured and bonding of thione and phosphine ligands with gold(I). The C-2 resonance of the ligands was shifted from 7 to 9 ppm when complexed suggesting ligand bonding through the thione group. Similar shifts were observed for other imidazolidine-2-thione-gold(I)-halide complexes.[8-11]

The difference in the chemical shift for the C-2 resonance[8-11] between the free ligand and the complex is 8.45 ppm for [(EtImt)AuCl], 5.76 ppm for [(EtImt)AuBr] and 9.68 ppm for [(EtImt)AuCN] suggesting a maximum *trans* influence of the CN$^-$ group on the C-2 resonance. This is in agreement with the ligand field strengths found for Cl$^-$, Br$^-$ and CN$^-$ for complex formation with transition metals. The same effects were observed for other complexes (*e.g.*, [(Diaz(AuCl]: 8.28 ppm; [(Diaz)AuCN]: 8.84 ppm). An examination of the C-2 resonances shows a shielding of 9.67 ppm for [(Diaz)AuCN] compared to 7.81 ppm for [(Imt)AuCN]. This is probably due to the hydrophobic character and the size of the ligand. Similar effects have been observed[15] for [(Imt)$_2$HgCl$_2$] which has a chemical shift difference of 6.99 ppm for the C-2 resonance, compared to 7.33 ppm for [(Diaz)$_2$HgCl$_2$].

The results presented here indicate that gold(I) cyanide can form stable complexes with sulfur-containing ligands such as thiols and thiones. The red blood cells which contain both types of ligands, *e.g.*, hemoglobin, glutathione and ergothionine, can also form complexes with gold drugs, including gold(I) cyanide.[16] This in turn will alter the metabolism of the gold drugs.

EXPERIMENTAL

Chemicals

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

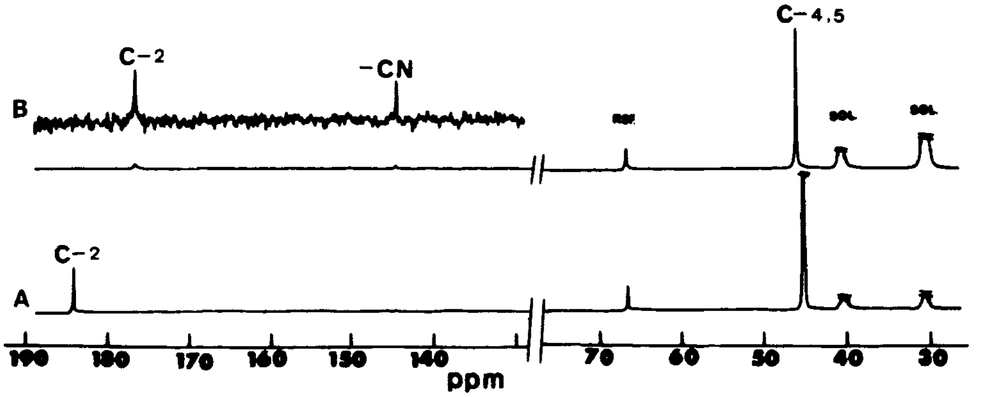

FIGURE 1 (A): ^{13}C NMR spectrum of the imidazolidine-2-thione ligand dissoved in 50/50 (v/v) DMSO/acetone. (B): ^{13}C NMR spectrum of the cyano-gold(I)-imidazolidine-2-thione complex dissolved in 50/50 (v/v) DMSO/acetone

TABLE III

^{13}C NMR Chemical Shifts of *N*-Alkyl-imidazolidine-2-thione-Gold(I)-CN Complexes†.

Complex	CN	C-2	C-4	C-5	R		
Imt		185.04	45.89	45.89			
[(Imt)AuCN]	144.05	177.23	45.16	45.16			
		(+7.81)	(+0.730)	(+0.73)			
EtImt		183.85	41.76	48.16	α-CH_2= 41.54	CH_3= 12.41	
[(EtImt)AuCN]	#	174.17	42.94	49.69	42.73	(12.69	
		(+9.68)	(-1.18)	(-1.53)	(-1.19)	(-0.28)	
PrImt		184.41	41.81	48.80	α-CH_2= 48.53	β-CH_2= 20.89,	CH_3= 11.48
[(PrImt)AuCN]	143.40	175.57	42.72	49.41	50.24	20.76	11.11
		(+8.84)	(-2.91)	(-0.61)	(−1.17)	(+0.13)	(+0.37)
IPrImt		183.38	41.92	43.06	α-CH= 46.72	CH_3= 19.38	
[(IprIm)AuCN]	144.28	173.83	42.81	44.72	49.01	19.98	
		(+9.55)	(-0.89)	(-1.66)	(-2.29)	(-0.60)	
Diaz		177.62	C-4, 6=40.82	20.25			
[(Diaz)AuCN]	145.35	167.95	41.17	19.231			
		(+9.67)	(-0.35)	(+1.02)			

† ^{13}C NMR resonances are assigned as given in R. Faure, E.J. Vincent, G. Assef, J. Kister and J. Metzger, *Org. Mgn. Res.*, 9, 688 (1977). The numbers in parentheses indicate shifts with respect to the free ligands. A positive value indicates high-field shift whereas a negative value shows a low field shift. #The resonance could not be detected in the spectrum.

Preparation of the complexes

The ligands were prepared by the method described in the literature.[17,18] AuCN was suspended in methanol, an equimolar amount of ligand was added, and the solution of these suspensions was stirred for 1 to 3 days. The AuCN was originally of a greenish colour, but gave a colourless solution after complexing with thiones. The solution was filtered, and after evaporation white crystalline complexes were obtained as listed in Table I. The *N*-methyl-imidazolidine-2-thione-Au-CN complex could not be prepared by this procedure.

Spectroscopic Measurements

The infrared spectra of all compounds were obtained on a Perkin-Elmer IR 180 using KBr pellets. The ^{13}C NMR spectra were obtained at 50.3 MHz on a Varian XL-200 NMR spectrometer using 50/50 (v/v) DMSO/acetone-d_6 solvents. The chemical shifts were measured using 1,4-dioxane which has a resonance at 67.4 ppm relative to DSS, as the internal reference.

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