Complexation of Captopril with Gold(I) and its Exchange Reactions with Thiomalate and Cyanide

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Captopril {Hcap, 1-[(2*S*)-3-mercapto-2-methylpropionyl]-L-proline} with gold(I) forms a 1:1 *crystalline* complex [Au(cap)]. The exchange reactions of thiomalate and cyanide with [Au(cap)] have been studied using ^{13}C NMR spectroscopy. It is found that [Au(cap)] forms a very high-molecular-weight polymer compared to gold(I) thiomalate. Thiomalate and CN^- both bind to [Au(cap)], however, as expected, CN^- binds more strongly. When $^{13}CN^-$ was added to [Au(cap)] solution, ^{13}C NMR resonances due to $[Au(cap)(^{13}CN)]^-$ (two isomers containing *cis* or *trans* cap) and $[Au(^{13}CN)_2]^-$ were observed. Evidence is presented which shows that the *cis* isomer of $[Au(cap)(^{13}CN)]^-$ is more stable than the *trans*.

Captopril, 1-[(2*S*)-3-mercapto-2-methylpropionyl]-L-proline, is a recently developed drug for the treatment of high blood pressure.[1-3] Its antihypertensive activity is thought to result from the inhibition of the angiotensin I-converting enzyme through binding of the thiol group to the active site.[1-4] The thiol group is also the key functional group in the metabolism of captopril, the major metabolites being captopril disulfide and mixed disulfide with thiols containing amino acids, peptides and proteins.[5-8]

Captopril exists in solution as an equilibrium mixture of *trans* and *cis* isomers with respect to the amide bond.[9,10] Carbon-13 NMR spectra give well resolved resonances for these isomers at various pH ranges.[9-13] It is therefore of interest to study the interaction of this ligand with heavy metal ions such as Zn^{2+}, Cd^{2+}, Cu^{2+}, Au^+, *etc.*,[13-15] using ^{13}C NMR spectroscopy.

Gold(I) has a strong but not exclusive tendency to form linear two-co-ordinate complexes, LAuX, where L is a neutral Lewis base (*e.g.* phosphine, thioether, thione, *etc.*) and X is an aryl or alkyl group, halide or pseudohalide.[16-21] With thiols such as cysteine, glutathione [*N*(*N*-L-γ-glutamyl-L-cysteinyl)glycine], penicillamine (3-mercaptovaline), *etc.*, it usually forms a polymer.[22-26] The gold(I) thiomalate [Au(tm)] and thioglucose [Au(tg)] complexes which are used as antiarthritic drugs also exist in polymeric form. By using various physical techniques the Au(tm) polymer was found to contain up to octamers.[23-27]

In this paper we describe the synthesis of the crystalline complex of gold(I) and captopril. As far as we know this is probably the first gold(I) thiolate complex found to be crystalline and in a subsequent study the single crystal structure determination will be reported. The main objective of this study is to see if captopril forms a similar complex with gold(I) as the Au(tm) polymer or whether it forms a 1:1 monomer. The exchange reactions of the complex with thiomalate, CN^- and $^{13}CN^-$ were also studied. Such exchange reactions are of interest because it was shown that the metabolism of gold drugs alters for smokers who absorbed HCN.[28-30]

Experimental

Chemicals.—Captopril was a gift from the Bristol Myors-Squibb Institute for Medical Research, Princeton, NJ, $K^{13}CN$ was obtained from MSD Isotope Division, Montreal, Canada, KCN, sodium tetrachloroaurate dihydrate, thiomalic acid, 99.7% D_2O, 40% NaOD in D_2O, and 35% DCl in D_2O from Fluka.

NMR Measurements.—The ^{13}C NMR spectra were recorded at 50.03 MHz on a Varian XL-200 spectrometer operating in the pulsed Fourier-transform mode. The measurements were carried out with coherent off-resonance ^1H decoupling or with broad-band ^1H decoupling. Chemical shifts were measured relative to internal dioxane or glycerol, δ 67.40 and 63.33 respectively upfield from $SiMe_4$. All spectra were recorded after 50 000–70 000 scans.

pH *Measurements.*—All pH measurements were made at 22 °C with a model 620 Fisher Accumet pH meter equipped with a Fisher microprobe combination pH electrode; pH* is used to indicate the actual meter reading for D_2O solutions with no correction for deuterium isotope effects.

Infrared Measurements.—Infrared spectra (4800–200 cm^{-1}) of the complex and ligand were recorded on a Perkin Elmer IR 180 spectrophotometer for KBr pellets.

Preparation of the Captopril–Gold(I) *Complex.*—A solution of 2,2'-thiodiethanol (thiodiglycol) (0.976 g, 8.0 mmol) in water (20 cm^3) was added dropwise to a constantly stirred solution of sodium tetrachloroaurate dihydrate (1.6 g, 4.0 mmol) in water (40 cm^3) maintained at 0 °C. After the mixture had become colourless (indicating complete reduction of Au^{III} to Au^I,[23] a solution of captopril (0.852 g, 4.0 mmol) in water (15 cm^3) was added. A white precipitate appeared which was washed twice with water and dried *in vacuo*. Yield 72.0%, m.p. 245 °C (Found: C, 25.30; H, 3.35; N, 3.15; S, 7.40. Calc. for $C_9H_{13}AuNNaO_3S$: C, 24.85; H, 3.00; N, 3.20; S, 7.35%).

The above procedure was repeated with the same mole ratios of captopril and $AuCl_4^-$ and a crystalline complex was obtained (Found: C, 25.8; H, 3.5; N, 3.1; S, 7.4%), yield 75%, m.p. 244 °C.

Resonance Assignments.—Structural formulae for gold thiomalate, sodium thiomalate and the isomers of captopril are as shown. The labels g_1 and g_2 are employed for resonances arising from the CH and CH_2 groups of glycerol.

The chemical shifts of the *cis* and *trans* isomers of captopril are given in Tables 1 and 2.

Results

Interaction of [Au(cap)] *with Thiomalate.*—The ^{13}C NMR spectrum of [Au(cap)] (0.25 mol dm^{-3} in D_2O) is shown in Fig. 1(*a*). The complex is insoluble in water below a pH* of 12 and only soluble at high pH*. Its colourless solution is very viscous and the ^{13}C NMR spectrum very broad.

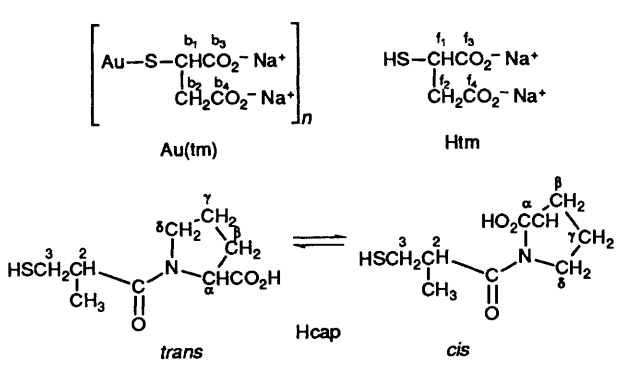

Table 1 Carbon-13 NMR chemical shifts of gold(I)–captopril and –thiomalate complexes at pH* 7.20

Assignment[a]		Free captopril and free Htm[a]	Au^{I}:captopril:Htm (1:1:2)
C^3	*trans*	27.72	*b*
	cis	27.56	*b*
C^2	*trans*	42.33	*b*
	cis	42.85	*b*
CH_3	*trans*	16.90	18.45, 17.40, 16.84
	cis	16.75	—
CON	*trans*	176.51	—
	cis	177.37	—
C_α	*trans*	62.55	62.58
	cis	63.21	63.17
C_β	*trans*	30.43	30.53
	cis	32.19	32.23
C_γ	*trans*	25.13	25.17
	cis	23.29	*b*
C_δ	*trans*	48.80	49.50
	cis	47.92	*b*
CO_2^-	*trans*	180.53	—
	cis	*b*	—
b_2	Au(tm)	—	47.96
b_1	Au(tm)	—	43.57
f_2	Htm	45.13	45.13
f_1	Htm	42.37	42.37

[a] From ref. 9. [b] Resonance is either too small to detect or overlapped with another resonance.

When 1 equivalent of solid thiomalate (0.25 mol dm^{-3}) was added to the aqueous solution of [Au(cap)] the pH* decreased and was adjusted to 7.20. A few captopril resonances appeared as shown in Fig. 1(*b*). Also thiomalate bound to gold(I), δ 47.96 (b_2) and 43.57 (b_1), appeared as did free thiomalate, δ 45.13 (f_2) and 42.37 (f_1). When a second equivalent of solid thiomalate (0.50 mol dm^{-3} total) was added to the [Au(cap)] solution the captopril resonances sharpened, a very small enhancement of resonances b_2 and b_1 was observed, and resonances f_2 and f_1 increased in intensity. These resonances of free and bound thiomalate show that it is in equilibrium with the [Au(cap)]. The chemical shifts of various [Au(cap)] resonances are given in Table 1.

Interaction of [Au(cap)] *with* CN^-.—Fig. 2(*a*) shows the spectrum of 0.25 mol dm^{-3} captopril at pH* 12.20. When 1 equivalent of KCN was added to the [Au(cap)] solution the captopril resonances appeared but they were broad (not shown in Fig. 2). The complex was soluble only above pH* 12.20. When another equivalent of KCN was added the captopril resonances became sharper [Fig. 2(*b*)]. Fig. 2(*c*) shows the spectrum of the same solution but with the pH* adjusted to 7.20. The resonances at δ 153.67 and 154.20 in Fig. 2(*b*) were assigned to $[Au(cap)(CN)]^-$ and $[Au(CN)_2]^-$ complexes at pH* 12.20.[31,32] These shifted to δ 154.09 and 155.38 at pH* 7.20. The chemical shifts of [Au(cap)] in the presence of CN^-

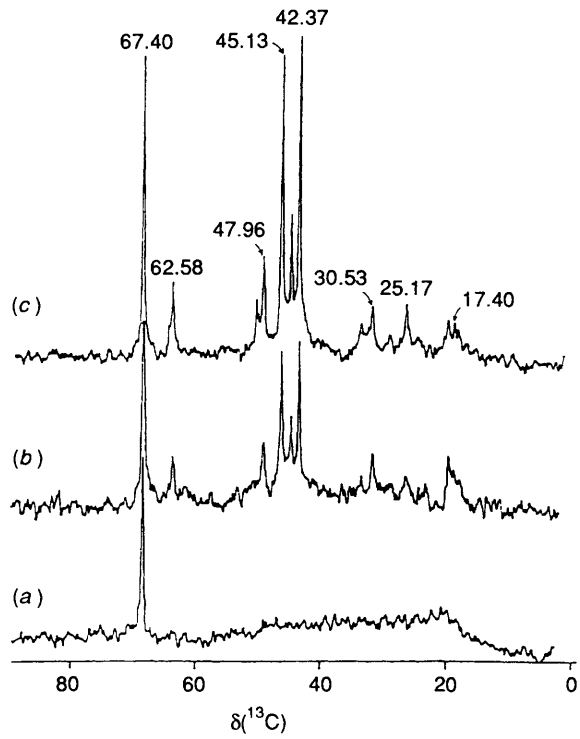

Fig. 1 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra of (*a*) 0.25 mol dm^{-3} [Au(cap)] at pH* 12.20, (*b*) 0.25 mol dm^{-3} [Au(cap)]: Htm at a 1:1 ratio at pH* 7.20, and (*c*) 0.25 mol dm^{-3} [Au(cap)]: Htm at a 1:2 ratio at pH* 7.20

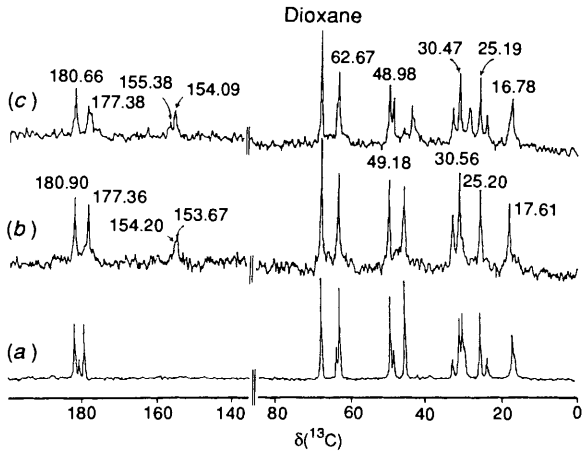

Fig. 2 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra of (*a*) 0.25 mol dm^{-3} captopril at pH* 12.20, (*b*) 0.25 mol dm^{-3} [Au(cap)]: CN^- at a 1:2 ratio at pH* 12.20, and (*c*) as (*b*) but at pH* 7.20

are given in Table 2. These assignments are based on similar studies carried out on CN^- with [Au(tm)] and gold(I)–glutathione.[31,32]

Figs. 1(*c*) and 2(*c*) show spectra at 1:2 ratio of [Au(cap)]:tm^- and [Au(cap)]:CN^- respectively for comparison.

Interaction of [Au(cap)] *with* $^{13}CN^-$.—Fig. 3(*a*) shows the spectrum (only the low-field region) of a freshly prepared (from the second batch) 0.50 mol dm^{-3} [Au(cap)] solution in D_2O. Again the solution was viscous and the complex dissolved only at high pH* *ca.* 13. When 0.125 mol equivalent of $K^{13}CN$ was added as a solid to the [Au(cap)] solution the resonances were broad in the high-field region. However, three intense resonances appeared in the low-field region, assigned on the basis of the mole ratio of the *cis* (c) and *trans* (t) isomers of captopril[9] as $[Au\{cap(c)\}(^{13}CN)]^-$, $[Au\{cap(t)\}(^{13}CN)]^-$ and

Table 2 Carbon-13 NMR chemical shifts of gold(I)–captopril and –cyanide complexes at pH* 12.20 and 7.20

Assignment[a]		Free captopril at pH* 12.20	[Au(cap)]:CN^- (1:2) at pH* 12.20	Free captopril at pH* 7.20	[Au(cap)]:CN^- (1:2) at pH* 7.20
C^3	*trans*	29.69	30.56	27.72	27.84
	cis	29.10	29.82	27.56	*b*
C^2	*trans*	44.83	45.15	42.33	42.39
	cis	*b*	*b*	42.85	42.92
CH_3	*trans*	16.75	17.61	16.90	16.78
	cis	16.09	16.28	16.75	*b*
CON	*trans*	178.50	177.36	176.51	176.80
	cis	179.26	*b*	177.37	177.38
C_α	*trans*	62.48	62.75	62.55	62.67
	cis	63.21	*b*	63.21	63.21
C_β	*trans*	30.50	30.56	30.43	30.47
	cis	32.26	32.38	32.19	32.19
C_γ	*trans*	25.13	25.20	25.13	25.19
	cis	23.29	*b*	23.29	23.33
C_δ	*trans*	48.80	49.18	48.80	48.98
	cis	47.77	*b*	47.92	47.91
CO_2^-	*trans*	181.06	180.90	180.53	180.66
	cis	180.92	*b*	*b*	*b*
$[Au(CN)_2]^-$		—	154.20	—	154.09
$[Au(cap)(CN)]^-$		—	153.67	—	155.38

[a] From ref. 9. [b] Resonance is either too small to detect or overlapped with another resonance.

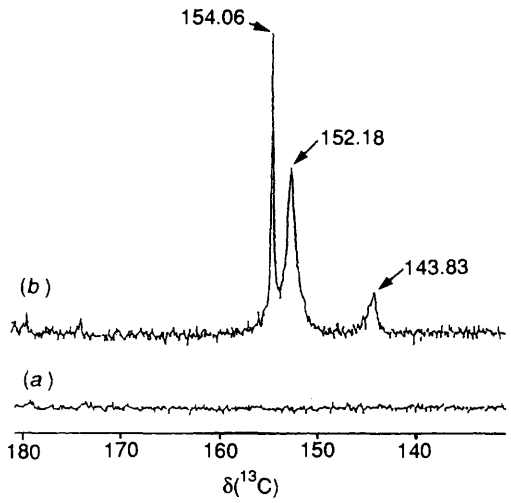

Fig. 3 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra in the low-field region of (*a*) 0.50 mol dm^{-3} [Au(cap)] at pH* 13.08, (*b*) 0.125 mol dm^{-3} 100% labelled $^{13}CN^-$ added to the [Au(cap)] solution at pH* 7.40

$[Au(^{13}CN)_2]^-$ at δ 143.83, 152.18 and 154.06 respectively. Assuming the T_1 values are about the same, from integration of the ^{13}C NMR resonances the relative amounts are 36% $[Au(^{13}CN)_2]^-$, 52% *trans* and 12% *cis* complex.

Since the three resonances in the low-field region were very intense compared to other captopril resonances, the whole experiment was repeated by addition of 10% labelled $^{13}CN^-$ and 90% unlabelled CN^- to the 0.50 mol dm^{-3} [Au(cap)] solution. As shown in Fig. 4(*b*)–4(*e*) (only the low-field region) the $[Au(CN)_2]^-$ resonance at δ 154.09 was sharp and increased in intensity. Also, as expected, as the concentration of $^{13}CN^-$ was increased the intensity of *cis* and *trans* $[Au(cap)(^{13}CN)]^-$ resonances increased. At a 1:1 ratio of [Au(cap)]:$^{13}CN^-$ the *cis* and *trans* isomers were in rapid exchange and the average resonance moved toward that of $[Au(^{13}CN)_2]^-$ to an extent that the *cis* complex seemed to disappear [Fig. 4(*e*)]. When the concentration of $^{13}CN^-$ was increased further a precipitate was formed. {Note in this experiment the concentrations of [Au(cap)] and CN^- are higher than in the first experiment.} The precipitate was filtered off and dissolved in $(CD_3)_2SO$. Only one resonance at δ 153.67 appeared in the ^{13}C NMR spectrum, due to the $[Au(^{13}CN)_2]^-$ complex.

The IR spectrum of the [Au(cap)] complex shows the absence of an SH absorption at 2500 cm^{-1}. This suggests that gold(I) binds *via* the thiol group of the ligand. An absorption at 345 cm^{-1} was assigned to Au–S, however there was no Au–Cl absorption within the 310–320 cm^{-1} region which eliminates the possibility of a $[Au(cap)Cl]^-$ complex.[19,20]

Discussion

Gold(I) is known to form polymers with thiols, from hexa-to octa-mers.[22–27] As shown in Figs. 1(*a*), 3(*a*) and 4(*a*), in the captopril system the ^{13}C NMR resonances are very broad and the solution very viscous, suggesting that a very high-molecular-weight polymer is formed.

Gold(I) thiomalate in the presence of Htm or other added thiols RSH usually forms $[Au(SR)_2]^-$ complexes.[33–36] As shown in Fig. 1(*b*) the resonances b_1 and b_2 at δ 47.96 and 43.57 appeared at a 1:1:1 ratio of Au^I:cap^-:tm^-. At a 1:1:2 ratio there was no significant change in the spectrum [Fig. 1(*c*)]. These results indicate that tm^- binds to the [Au(cap)] complex but does not displace all the captopril to form a $[Au(tm)_2]^-$ complex. The displaced captopril is in rapid exchange with gold(I) and therefore only the exchange-averaged resonances are observed. These resonances may be due to the various species present, such as $[Au(cap)(tm)]^-$, $[Au(cap)_2]^-$, *etc.*

As noted in Table 1 and shown in Fig. 1(*c*), various CH_3 resonances are observed for captopril in the presence of thiomalate. These resonances arise from the $[Au(cap)(tm)]^-$ as well as $[Au(cap)_2]^-$ species present in solution. However, the [Au(cap)] polymer is too strong to be broken by the excess of thiomalate and therefore the resonances for the different species could not be resolved.

Cyanide binds to Au^I very strongly, the formation constant for $[Au(CN)_2]^-$ being $\log \beta_2$ 36.6.[32,37] When KCN was added to [Au(cap)] solution, at a 1:1 ratio, the resulting ^{13}C NMR resonances were broad; however, at a 1:1:2 ratio of Au^I:cap^-:CN^- the resonances of captopril were sharper as shown in Fig. 2(*c*). Note that the $[Au(cap)(CN)]^-$ complex at a 1:1:1 ratio was soluble at pH* 12.20, however at a 1:1:2 ratio the complex was soluble even at pH* 7.20, suggesting the formation of $[Au(CN)_2]^-$ which is soluble even at neutral pH*.[31,32]

The equilibrium competition of HCN and thiols (RSH)

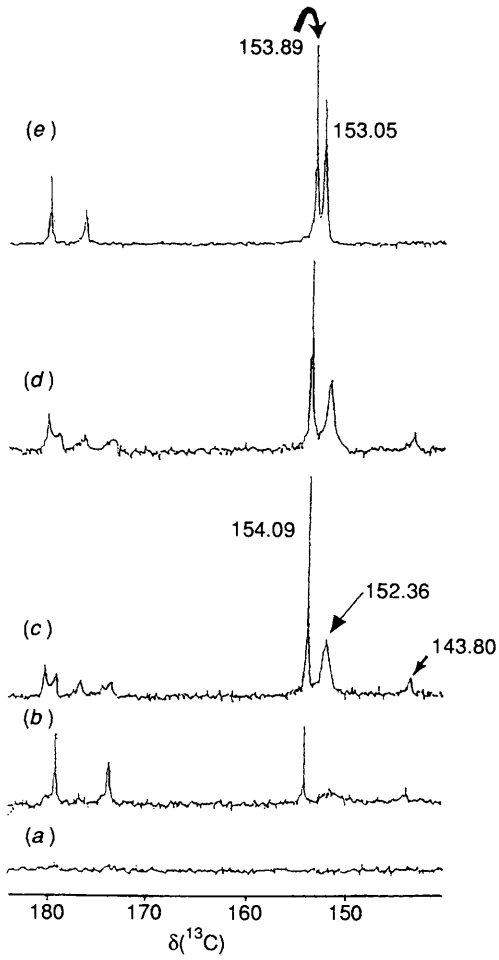

Fig. 4 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra in the low-field region of (*a*) 0.50 mol dm^{-3} [Au(cap)] at pH* 13.08; (*b*)–(*e*) show the effect of the addition of 10% labelled $^{13}CN^-$ and 90% unlabelled CN^- to 0.50 mol dm^{-3} [Au(cap)] at a [Au(cap)]:CN^- ratio of 8:1 at pH* 7.35, 8:3 at pH* 7.50, 8:4 at pH* 7.50, and 8:8 at pH* 7.60, respectively

for gold(I) favours cyanide and mixed-ligand complexes $[Au(SR)(CN)]^-$ which disproportionate to $[Au(SR)_2]^-$ and $[Au(CN)_2]^-$.[31,32] Such disproportionation is also observed in trialkyl- and triaryl-cyano(phosphine)aurate(I) complexes.[38,39]

Recently, we have reported the reaction between HCN and [Au(alb)(PEt_3)] (Halb = albumin). The gold(I) forms a three-co-ordinate transition complex (associative mechanism) which then gives the products $[Au(CN)_2]^-$, [Au(alb)X] where (X is an unknown ligand) and $OPEt_3$. Cyanide displaced both Halb and PEt_3 ligands. Various cyanogold(I)–trialkylphosphine or –triarylphosphine complexes disproportionate to give $[Au(CN)_2]^-$ and bis(trialkyl- or triaryl-phosphine)gold(I) complexes.[38–40] In similar studies[41] it was found that when [Au(tg)] reacted with $^{13}CN^-$ it gave a mixture of $[Au(CN)_2]^-$ and [Au(tg)(CN)]$^-$ at ratios of [Au(tg)]:CN^- up to 1:2; at the ratio 1:2 $[Au(CN)_2]^-$ was the only species formed. The affinity of ligands for gold(I) is found to be in the order $CN^- \gg PEt_3$ > Halb > thiols.[40]

The two resonances observed in the ^{13}C NMR spectrum of [Au(cap)] and CN^- at 1:1 ratio, at δ 155.38 and 154.09, are due to the $[Au(CN)_2]^-$ and [Au(cap)(CN)]$^-$ [Fig. 2(*b*) and 2(*c*)]. In the high-field region δ 0–70 the resonances are not well resolved. This may be due to the formation of various species which are in equilibrium, such as [Au(cap)], [Au(cap)(CN)]$^-$ and $[Au(cap)_2]^-$.

In the presence of $^{13}CN^-$ the [Au(cap)] complex gave two distinct isomers. The resonance of $[Au\{cap(t)\}(^{13}CN)]^-$ is at lower field compared to the corresponding *cis* (c) isomer. The assignment of these two resonances is based on the mole ratio of the free captopril isomers present in solution. In previous studies, we found that the formation constant of the *cis* isomer of [Hg(cap)Me] was greater than that of the *trans*.[10] The relative positions of the resonances of the [Au(cap)(^{13}CN)]$^-$ isomers can be explained in terms of their stabilities. Thus the d_π–p_π back bonding in the *cis* isomer will be greater than that of the *trans* which in turn will shift the $^{13}CN^-$ resonance upfield.[42]

In conclusion the results presented indicate that captopril binds to gold(I) strongly and forms a very high-molecular-weight polymer compared to [Au(tm)]. Both thiomalate and CN^- bind to [Au(cap)], but CN^- binds more strongly. The *cis* isomer of [Au(cap)(^{13}CN)]$^-$ is found to be more stable than the *trans*, based on the ^{13}C NMR chemical shifts.

Acknowledgements

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