Carbon-13 Nuclear Magnetic Resonance Studies of the Redox Reactions of Aurothiomalates with Selenocyanate in Aqueous Solution

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The interactions of SCN^- and $SeCN^-$ with aurothiomalate $[Au(tm)]_n$ in aqueous solution were studied by ^{13}C NMR spectroscopy. The $[Au(tm)]_n$ is further polymerized in the presence of SCN^-, however, $SeCN^-$ binds to $[Au(tm)]_n$ forming monomeric $[Au(SeCN)(tm)]^-$. This complex initially disproportionates to give $[Au(SeCN)_2]^-$ and $[Au(tm)_2]^-$. The $[Au(SeCN)_2]^-$ eventually decomposed to give $[Au(CN)_2]^-$ and metallic selenium. The free tm^- released from $[Au(tm)]_n$ is oxidized to the thiomalic disulfide $(tm)_2$. When the bis complex $[Au(tm)_2]^-$ reacted with $SeCN^-$ it did not form $[Au(SeCN)(tm)]^-$, but instead gave $(tm)_2$, $[Au(CN)_2]^-$ and Se_2^{2-}.

Gold(I) thiolates have been used successfully over many years in the treatment of rheumatoid arthritis[1–3] and such compounds, *e.g.* aurothiomalate 'Myochrysin' [Au(tm)], aurothioglucose, *etc.* are formulated as simple monomers. Gold(I) usually forms linear two-co-ordinate complexes but not in the case of gold(I) thiolates. In order to attain a linear co-ordination, these drugs exist as polymers.[1–3] The polymerization of $[Au(tm)]_n$ has been identified using various physical techniques[2–6] and the extent of polymerization is reported to be dependent on the concentrations of the $[Au(tm)]_n$, salts and pH of the solution.[7]

In the presence of thiols (HSR) and thiones (L) these drugs bind to form bis complexes, *e.g.* $[Au(SR)_2]^-$ and [AuL(SR)].[8–11] The binding of selenopropionate with $[Au(tm)]_n$ has also been studied[12] and a bis(selenopropionato)gold complex is formed. Although the redox reactions of gold(I)–gold(III) with polyselenide have been studied extensively,[13–15] very little work has been done concerning the interaction of these gold drugs with selenium-containing ligands.

The reactions of CN^- and SCN^- with gold(I) thiolates are important since it has been reported that chrysotherapy patients who are tobacco smokers accumulate gold in their red blood cells from gold-based drugs, while non-smokers do not.[16–18] This was attributed to cyanide from the inhaled smoke which alters the metabolism of the gold-containing drugs, because it binds with gold(I) to form $[Au(CN)_2]^-$. The log β_2 value for $[Au(CN)_2]^-$ is reported to be 36.6.[19] The CN^- is known to undergo two reactions: reversible binding to met-haemoglobin and irreversible oxidation to thiocyanate.[20] If the CN^- generated by smokers in the red blood cells is oxidized to thiocyanate, it is important to know whether an interaction between $[Au(tm)]_n$ and SCN^- occurs or not and as such we have investigated the interaction of KSCN with $[Au(tm)]_n$. Comparative reactions between KSeCN and $[Au(tm)]_n$ and between $KSe^{13}CN$ and $[Au(tm)_2]^-$ using ^{13}C NMR spectroscopy have also been studied. To the best of our knowledge this is the first study in which the disproportionation and redox reactions of $[Au(SeCN)(tm)]^-$ are reported.

Experimental

Chemicals.—The compounds KSCN, KSeCN and $[Au(tm)]_n$ were obtained from ICN K and K Labs, Plainview, New York, 99.7% D_2O, 40% NaOD in D_2O and 35% DCl in D_2O from Fluka and $KSe^{13}CN$ from Merck, Sharp and Dohme, Canada. The $[Au(tm)]_n$ was analysed as $[Au(tm)]\cdot0.33$ glycerol$\cdot H_2O$.[7]

NMR Measurements.—The ^{13}C NMR spectra were measured at 50.3 MHz on a Varian XL-200 spectrometer operating in the pulsed Fourier-transform mode. The measurements were made with coherent off-resonance ^1H decoupling or with broad-band ^1H decoupling. Chemical shifts were measured relative to the CH_2 resonance of internal glycerol (g_2) at δ 63.33 from $SiMe_4$. The probe temperature was 20 °C.

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 without correction for deuterium isotope effects.

Resonance Assignments.—The ^{13}C NMR resonance assignments of the gold(I) thiomalate complexes $[Au(tm)]_n$ and $[Au(tm)_2]^-$, the thiomalic disulfide $(tm)_2$ and $[Au(SeCN)(tm)]^-$ and their chemical shifts are given in Table 1.

Results

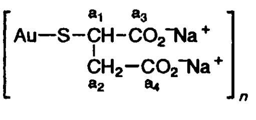
Experiment 1.—Fig. 1(*a*) shows the ^{13}C NMR spectrum of 0.20 mol dm^{-3} $[Au(tm)]_n$ in D_2O (2.0 cm^3) at pH* 7.40. The solution was pale yellow and the chemical shifts of various resonances are summarized in Tables 1 and 2. When 0.20 mol dm^{-3} KSCN was added as a solid (not shown in Fig. 1) no change in the spectrum was observed. The concentration of KSCN was then increased to 0.60 mol dm^{-3} and as shown in Fig. 1(*b*) (pH* 7.40), one resonance, labelled as p_1 at δ 49.0 appeared and a slight shift of a_1 (δ 47.9 to 47.4) was observed. In the low-field region there was no change in the chemical shifts

Table 1 Carbon-13 NMR chemical shifts and assignments

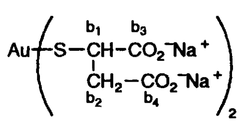
Species	δ (resonance assignment)
$[Au(tm)]_n$	47.9 (a_1 and a_2), 182.2 (a_3), 179.6 (a_4)
$[Au(tm)_2]^-$	43.3 (b_1), 47.7 (b_2), 184.7 (b_3), 184.8 (b_4)
$(tm)_2$	54.3 and 54.0 (d_1), 41.1 (d_2), 180.0 (d_3), 179.1 (d_4)
$[Au(SeCN)(tm)]^-$	42.0 (s_2), 52.8 (s_1); s_3 and s_4 overlapping with d_3 and d_4
$Se^{13}CN^-$	121.1
$[Au(^{13}CN)_2]^-$	154.0

Table 2 Carbon-13 NMR chemical shifts (δ) of 0.20 mol dm^{-3} $[Au(tm)]_n$ and in the presence of KSCN as shown in Fig. 1; concentrations in mol dm^{-3}

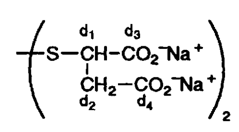
Fig.	$[Au(tm)]_n$: KSCN	a_1	a_2	a_3	a_4	SCN^-	p_1	p_2
1(*a*)	0.20:0.00	47.9	47.9	182.2	179.6	—	—	—
Not shown	0.20:0.20	47.9	47.9	182.2	179.6	133.4	—	—
1(*b*)	0.20:0.60	47.4	47.9	182.2	179.6	134.2	49.0	180.8
1(*c*)	0.00:0.20	—	—	—	—	133.4	—	—


$$[\mathrm{Au{-}S{-}CH(CO_2^-Na^+){-}CH_2{-}CO_2^-Na^+}]_n$$

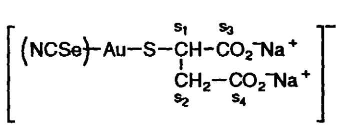
$[Au(tm)]_n$ (tm^- = Thiomalate)


$$\mathrm{Au}\left(\mathrm{S{-}CH(CO_2^-Na^+){-}CH_2{-}CO_2^-Na^+}\right)_2$$

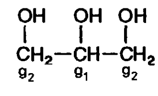
$[Au(tm)_2]^-$


$$\left(\mathrm{S{-}CH(CO_2^-Na^+){-}CH_2{-}CO_2^-Na^+}\right)_2$$

$(tm)_2$


$$[(\mathrm{NCSe}){-}\mathrm{Au{-}S{-}CH(CO_2^-Na^+){-}CH_2{-}CO_2^-Na^+}]^-$$

$[Au(SeCN)(tm)]^-$


$$\mathrm{CH_2(OH){-}CH(OH){-}CH_2(OH)}$$

Glycerol

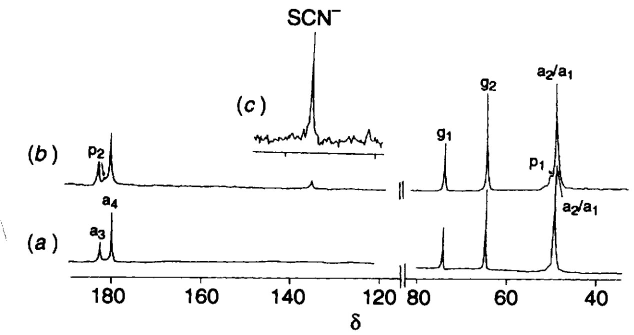


Fig. 1 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol dm^{-3} $[Au(tm)]_n$, (*b*) 0.20 mol dm^{-3} $[Au(tm)]_n$: 0.60 mol dm^{-3} KSCN and (*c*) 0.00 mol dm^{-3} $[Au(tm)]_n$: 0.20 mol dm^{-3} KSCN

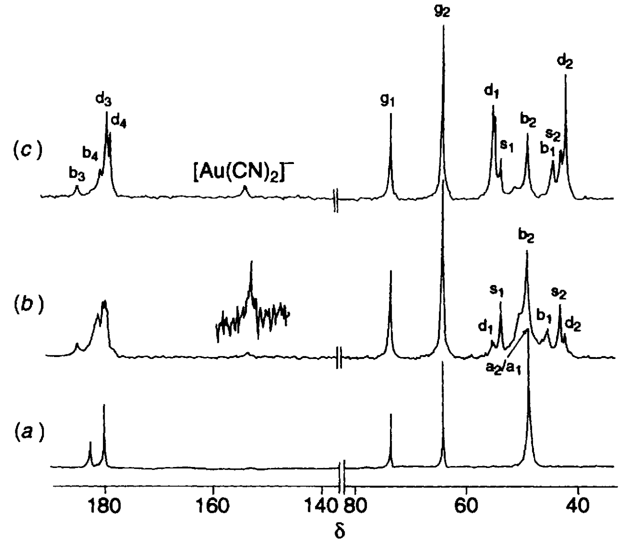


Fig. 2 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol dm^{-3} $[Au(tm)]_n$, (*b*) 0.20 mol dm^{-3} $[Au(tm)]_n$: 0.05 mol dm^{-3} KSeCN and (*c*) 0.20 mol dm^{-3} $[Au(tm)]_n$: 0.10 mol dm^{-3} KSeCN

observed for resonances a_3 and a_4, however, a new resonance p_2 appeared[7] at δ 180.8. The free SCN^- resonances appeared at δ 133.4 while in the presence of Au(tm) : SCN^- (1 : 3) it appeared at δ 134.2. The solution remained pale yellow throughout the experiment. Note that resonances a_1, a_2, a_3 and a_4 are assigned to $[Au(tm)]_n$ only. Once the tm^- binds to the *trans* side of $[Au(tm)]_n$ then a_1, a_2, a_3 and a_4 are denoted by b_1, b_2, b_3 and b_4. The assignment of these resonances are described elsewhere.[7-9]

Experiment 2.—Fig. 2(*a*) is similar to Fig. 1(*a*) {0.20 mol dm^{-3} $[Au(tm)]_n$ in D_2O} and all the conditions are the same. When 0.0144 g (equivalent to 0.050 mol dm^{-3}) of $SeCN^-$ was added as a solid to the $[Au(tm)]_n$ solution under N_2 gas {0.25 : 1 $SeCN^-$: $[Au(tm)]_n$ equivalent ratio}, the solution changed to orange. The chemical shifts of various resonances are summarized in Tables 1 and 3. Note that two new resonances, d_2 at δ 41.1 and d_1 at δ 54.3 and 54.0, appeared. The two peaks for d_1 are attributed to the diastereotopic CH carbons of two thiomalic disulfide diastereoisomers. The disulfide resonances were assigned by oxidizing free thiomalate (Htm) with O_2 at pH* 7.40.

The complex $[Au(SeCN)(tm)]^-$ also gave two resonances in the high-field region due to the CH (s_1) and CH_2 (s_2) groups at δ 52.8 and 42.0 respectively. The resonance for free $SeCN^-$ in D_2O (pH* 7.50) was also observed at δ 121.1.

When the concentration of $SeCN^-$ was increased to 0.10 mol dm^{-3} {0.5 : 1 $SeCN^-$: $[Au(tm)]_n$ equivalent ratio}, the solution became dark orange. The spectrum was recorded after overnight FID (free-induction decay) accumulation. The mixture contained some dark red precipitates (which is a characteristic of metallic selenium) and some metallic gold on the side of the NMR tube. As shown in Fig. 2(*c*), resonances d_2 and d_1 increased in intensity, while the opposite was observed for resonances s_2, s_1, b_2 and b_1. The precipitation of selenium and the deposition of metallic gold is explained by equations (1) and (2).

$$[Au(tm)] + SeCN^- \longrightarrow [Au(SeCN)(tm)]^- \qquad (1)$$

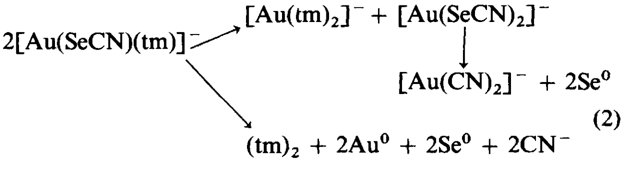

$$2[Au(SeCN)(tm)]^- \longrightarrow [Au(tm)_2]^- + [Au(SeCN)_2]^-;\quad [Au(SeCN)_2]^- \longrightarrow [Au(CN)_2]^- + 2Se^0$$
$$2[Au(SeCN)(tm)]^- \longrightarrow (tm)_2 + 2Au^0 + 2Se^0 + 2CN^- \qquad (2)$$

Table 3 Carbon-13 NMR chemical shifts (δ) of 0.20 mol dm^{-3} [Au(tm)]$_n$ and in the presence of KSeCN as shown in Fig. 2; concentrations in mol dm^{-3}

Fig.	[Au(tm)]$_n$: KSeCN	b_1	b_2	b_3	b_4	s_1	s_2	d_1	d_2	d_3	d_4	[Au(CN)$_2$]$^-$
2(*a*)	0.20:0.00	Chemical shifts are same as in Table 2, Fig. 1(*a*)										
2(*b*)	0.20:0.05	43.3	47.9	185.0	181.0	52.8	42.0	54.3 54.0	41.1	180.0	179.1	155.3
2(*c*)	0.20:0.10	The chemical shifts of various resonances remained unchanged in Fig. 2(*b*) and 2(*c*), however, their intensities changed										

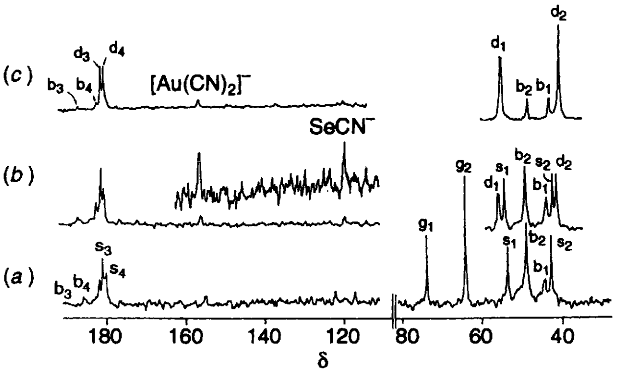


Fig. 3 The 50 MHz ^{1}H noise-decoupled ^{13}C NMR spectra (at pH* 7.40) of 0.20 mol dm^{-3} [Au(tm)]$_n$: 0.20 mol dm^{-3} KSeCN: (*a*) after 6 h, (*b*) after 12 h and (*c*) after 24 h

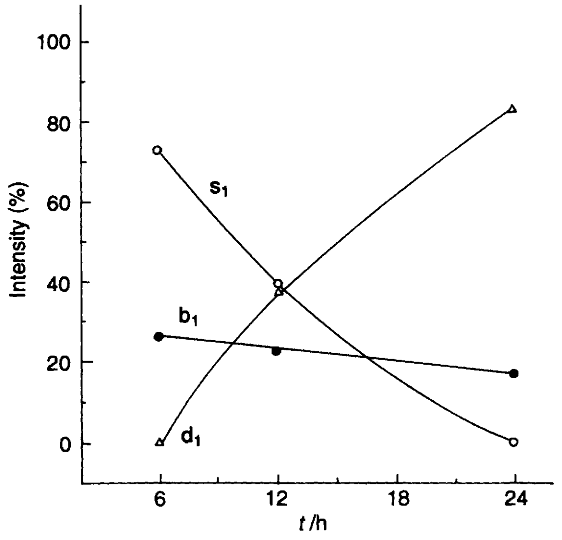


Fig. 4 The (%) intensity of the CH resonance of tm$^-$ as a function of time (for resonance assignment see text)

Experiment 3.—In order to follow the time-dependent disproportionation of the unstable complex [Au(SeCN)(tm)]$^-$ the following experiment was carried out.

Dinitrogen gas was passed through a 0.20 mol dm^{-3} [Au(tm)]$_n$ solution in D$_2$O, pH* 7.40, and 1 equivalent of solid SeCN$^-$ was added. The solution was slightly brown and no precipitates were observed. The spectrum shown in Fig. 3(*a*) was recorded after 6 h. Resonances b_4, b_3, b_2, b_1, s_4, s_3, s_2 and s_1 appeared and their chemical shifts are given in Table 4. It should be noted that there are no signs of resonances of the thiomalic disulfide (tm)$_2$ in this spectrum. The spectrum in Fig. 3(*b*) was recorded after 12 h; the solution was dark brown and some precipitates were observed, due to metallic gold and selenium. This time resonances from (tm)$_2$ (d_2 and d_1) were also present in the spectrum. The resonances at δ 155.3 is presumably due to [Au(^{13}CN)$_2$]$^-$ as described in equation (2) while that at δ 121.2 is due to free SeCN$^-$. Fig. 3(*c*) was recorded after 24 h; the solution was still dark brown and more precipitates of metallic gold and selenium appeared. The resonances s_2 and s_1 disappeared completely and d_2 and d_1 increased in intensity relative to g_2 of glycerol.

Fig. 4 shows the approximate percentage intensity of resonances b_1, d_1 and s_1 from the spectra of Fig. 3(*a*)–(*c*). The values are measured relative to g_2. The T_1 values of these resonances were not measured owing to the instability of [Au(SeCN)(tm)]$^-$. However, the percentage values show how the disproportionation or decomposition of [Au(SeCN)(tm)]$^-$ proceeds with time.

Experiment 4.—In order to assign the resonance at δ 153.18, the following experiment was carried out. A 0.20 mol dm^{-3} [Au(tm)]$_n$ solution was prepared in D$_2$O (1 cm^3) under N$_2$ gas and 1 equivalent of KSe^{13}CN (0.0290 g KSe^{13}CN) was added. A broad resonance at δ 153.18 and a sharp resonance at δ 121.16 due to unreacted Se^{13}CN$^-$ appeared. Since the Se^{13}CN$^-$ used was labelled, the higher-field resonances were very weak. Two separate resonances due to [Au(SeCN)$_2$]$^-$ and [Au(SeCN)(tm)]$^-$ were anticipated, however, only one broad resonance at δ 153.18 was observed. This may be due to the exchange between these two species. However, as shown in equation (2) both species eventually decomposed to give [Au(CN)$_2$]$^-$. Therefore the resonance at δ 153.18 must be due to [Au(CN)$_2$]$^-$ because it did not disappear even after 24 h of NMR data accumulation.

Experiment 5.—To confirm the assignment of resonances s_1 and s_2, the following experiment was carried out. A 0.20 mol dm^{-3} [Au(tm)]$_n$ solution (pH* 7.40) was prepared in D$_2$O (1 cm^3) under N$_2$ gas and 0.75 equivalent of tm$^-$ (0.0225 g Htm) was added. The solution was pale yellow. The Au : tm$^-$ ratio was 1 : 1.75, and the tm$^-$ concentration was kept at less than two per gold because [Au(tm)]$_n$ itself contains about 10% tm$^-$ as a free ligand and as such the actual species would be [Au(tm)$_2$]$^-$ in aqueous solution.[21] As shown in Fig. 5(*a*), no free tm$^-$ resonances appeared. The resonance assignments are given in Tables 1 and 5. One equivalent of KSe^{13}CN (0.0290 g KSe^{13}CN) was added to the solution. The colour did not change immediately, but after 12 h of NMR data accumulation it changed to dark brown. The spectrum is shown in Fig. 5(*b*). It should be noted that no s_1 or s_2 resonances appeared in the spectrum, only d_1 and d_2. A sharp resonance appeared at δ 154.06, due to [Au(CN)$_2$]$^-$ and a resonance at δ 121.13 due to free Se^{13}CN$^-$ is also observed. Another spectrum was recorded after 24 h of accumulation [Fig. 5(*c*)]. Note that compared to g_2, the resonances d_1, d_2 increased in intensity and b_1, b_2 decreased in intensity.

Discussion

Experiment 1 involved the interaction between SCN$^-$ and [Au(tm)]$_n$. The extra peaks p_1 and p_2 appeared in the presence of SCN^-. Similar peaks were observed when NaCl or Na_2SO_4 was added to $[Au(tm)]_n$ solution, which shows that SCN^- is acting as a salt and is further polymerizing the $[Au(tm)]_n$ solution as described earlier.[7]

The results of experiment 2 indicate that the reaction of $SeCN^-$ with $[Au(tm)]_n$ generates $[Au(SeCN)(tm)]^-$ in aqueous solution as shown in equation (1). The assignments of resonances b_1, b_2, b_3 and b_4 have been described previously.[8] The assignments of d_1, d_2, d_3 and d_4 were confirmed by dissolving Htm in D_2O at pH* 7.4 and oxidizing it with air. The resonances d_2 and d_1 were assigned by off-resonance decoupling and s_1 and s_2, which appeared after the addition of $SeCN^-$ to the $[Au(tm)]_n$ solution, must be from $[Au(SeCN)(tm)]^-$ as described in equation (1). As reported in the literature,[22] most $SeCN^-$-containing complexes decompose in aqueous solution in the presence of a majority of metal ions. The resonances s_3 and s_4 of $[Au(SeCN)(tm)]^-$ were observed, but overlapping with d_3 and d_4.

The attempt to generate $[Au(SeCN)_2]^-$ by reducing gold(III) to gold(I) in aqueous solution and then adding $SeCN^-$ failed and only brown precipitates with gold(I) were observed.

The disproportionation of asymmetric linear gold(I) complexes is known,[23–26] for example as shown in equation (3) (where RS^- = thiomalate, thioglucose, glutathione *etc.*).

$$2[Au(CN)(RS)]^- \rightleftharpoons [Au(RS)_2]^- + [Au(CN)_2]^- \quad (3)$$

Scrambling reactions of cyano(trialkylphosphine)gold(I) complexes, similar to equation (3), have also been revealed by ^{13}C, ^{15}N and ^{31}P NMR spectroscopy,[27–29] equation (4) (where R = methyl, ethyl, phenyl *etc.*).

$$2[Au(CN)(PR_3)] \rightleftharpoons [Au(PR_3)_2]^+ + [Au(CN)_2]^- \quad (4)$$

However, the asymmetric complex $[Au(SeCN)(tm)]^-$ does not disproportionate according to the reaction described in equation (3) because, if it did, an increase in intensity of resonance b_1 and a decrease in intensity of s_1 should have been observed. However, as shown in Figs. 3 and 4 and described in experiments 3 and 4 the intensity of resonance b_1 does not change, but s_1 transforms directly to d_1. Moreover the intensity of resonance b_1 of $[Au(tm)_2]^-$ did not change significantly indicating that $[Au(tm)_2]^-$ is stable over a 6–24 h period.

Recently a study on the exchange reactions of $[Au(tm)]_n$ with selenopropionate in water was reported.[12] At a 1 : 2 ratio of $[Au(tm)]_n$: selenopropionate the bis(selenopropionato)gold complex is formed. The Htm was ejected as a free ligand and unlike in the present study, it did not oxidize to $(tm)_2$. This observation suggests that selenol simply binds to gold(I) and no redox reaction takes place. Similar reactions were observed with other selenols.[30] However when $[Au(tm)]_n$ was treated with thiourea a ternary complex was formed. When selenourea was added to $[Au(tm)]_n$, a redox reaction converting the gold(I) to metallic gold and thiomalic acid to the thiomalic disulfide $(tm)_2$ was observed.[31]

The resonances s_1 and s_2 were confirmed (experiment 5) by reacting $Se^{13}CN^-$ with $[Au(tm)_2]^-$ in which the intermediate species $[Au(SeCN)(tm)]^-$ was not generated because the gold(I) is blocked on both sides by tm^-, however, only the disulfide resonances of $(tm)_2$ appeared as shown in Fig. 5. The sharp resonance at δ 154.06 in Fig. 5(*c*) is due to $[Au(^{13}CN)_2]^-$.[23–25] This is simply because no $[Au(SeCN)(tm)]^-$ was generated and $[Au(Se^{13}CN)_2]^-$ is unstable and could not be observed even after 24 h as shown in Fig. 5(*c*). The $[Au(^{13}CN)_2]^-$ species may be generated as shown in equation (2). The resonance for $[Au(^{13}CN)_2]^-$ was observed at δ 154.00 in various studies of gold(I) drugs with CN^- interactions.[22–25]

In all our studies we observed an orange solution, which may be due to the generation of the Se_2^{2-} species which is known to be orange.[13–15]

The reaction between $[Au(tm)_2]^-$ and $SeCN^-$ without the formation of the intermediate species $[Au(SeCN)(tm)]^-$ is

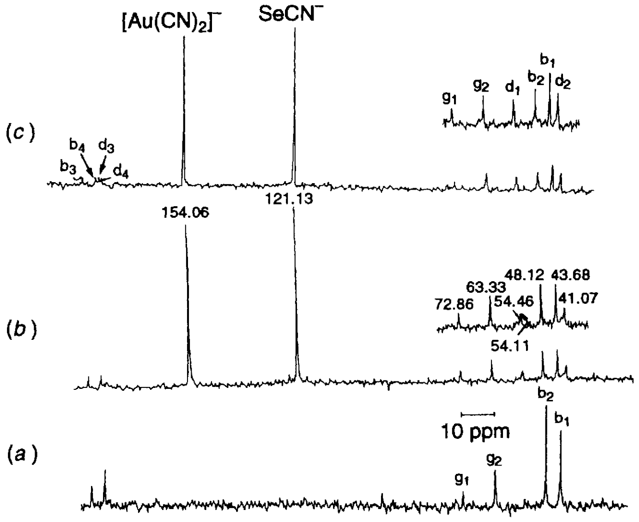


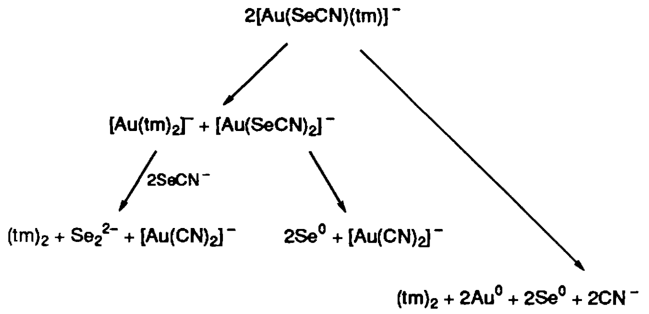
Fig. 5 The 50 MHz ^1H noise-decoupled ^{13}C NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol dm^{-3} $[Au(tm)]_n$: 0.15 mol dm^{-3} Htm; (*b*) as (*a*) + 0.20 mol dm^{-3} $KSe^{13}CN$, spectrum recorded after 12 h, and (*c*) as (*b*) but after 24 h of accumulation

Table 4 Carbon-13 NMR chemical shifts (δ) of 0.20 mol dm^{-3} $[Au(tm)]_n$: 0.20 mol dm^{-3} KSeCN as shown in Fig. 3

Fig.	*t*/h	b_1	b_2	b_3	b_4	s_1	s_2	s_3	s_4	d_1	d_2	d_3	d_4	$[Au(CN)_2]^-$
3(*a*)	6	43.7	47.9	185.0	181.0	52.8	42.0	180.0	179.1	—	—	—	—	—
3(*b*)	12	43.7	47.9	185.0	181.0	52.8	42.0	180.0	179.1	54.3 54.0	41.1	180.0	179.1	155.3
3(*c*)	24	43.7	47.9	185.0	181.0	—	—	—	—	54.3 54.0	41.1	180.0	179.1	155.3

Table 5 Carbon-13 NMR chemical shifts (δ) of 0.20 mol dm^{-3} $[Au(tm)_2]^-$ and in the presence of $KSe^{13}CN$ as shown in Fig. 5; concentrations in mol dm^{-3}

Fig.	$[Au(tm)_2]^-$: $KSe^{13}CN$	*t*/h	b_1	b_2	b_3	b_4	d_1	d_2	d_3	d_4	$[Au(CN)_2]^-$	$Se^{13}CN^-$
5(*a*)	0.20 : 0.00		43.28	47.71	184.65	180.76	—	—	—	—	—	—
5(*b*)	0.20 : 0.20	12	43.68	48.12	184.65	180.76	54.46 54.11	41.07	180.0	179.1	154.06	121.13
5(*c*)	0.20 : 0.20	24	The chemical shifts of various resonances remained unchanged in Fig. 5(*b*) and (*c*) however, their intensities changed									



Scheme 1

explained by equation (5). The $[Au(CN)_2]^-$ and Se_2^{2-} species

$$[Au(tm)_2]^- + 2SeCN^- \rightleftharpoons (tm)_2 + Se_2^{2-} + [Au(CN)_2]^- \quad (5)$$

generated explain the orange solution as well as a sharp resonance [Fig. 5(*b*) and (*c*)] at δ 154.00 which is clearly due to $[Au(CN)_2]^-$.[24–27]

Reactions (2)–(5) are summarized in Scheme 1. The final products lead to $(tm)_2$, $[Au(CN)_2]^-$, an orange colouration solution due to Se_2^{2-}, metallic gold, metallic selenium and free CN^-. This free CN^-, which may be generated in small concentrations may exchange further with $[Au(CN)_2]^-$. This exchange reaction will lead to a slight shift of the $[Au(CN)_2]^-$ resonance between δ 153.0 and 155.0 together with broadening of the resonance.[24–26]

Conclusion

The present study shows that SCN^- increases the polymerization of $[Au(tm)]_n$. However, $SeCN^-$ oxidizes thiomalic acid to the thiomalic disulfide and reduces gold(I) to metallic gold for both $[Au(tm)]_n$ and $[Au(tm)_2]^-$. Similar observations were made[31] when $[Au(tm)]_n$ was treated with thio- and seleno-urea. Therefore it can be concluded that selenium is essential for these redox reactions.

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