# 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 $\beta_2$ value for $[Au(CN)_2]^-$ is reported to be 36.6.[19] The $CN^-$ is known to undergo two reactions: reversible binding to methaemoglobin 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 $[Au(tm)]\cdot 0.33\,glycerol\cdot H_2O$.[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

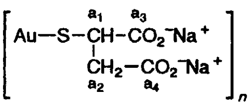
*Experiment* 1.—Fig. 1(*a*) shows the $^{13}C$ NMR spectrum of 0.20 mol $dm^{-3}$ $[Au(tm)]_n$ in $D_2O$ (2.0 $cm^3$) at pH* 7.40. The solution was pale yellow and the chemical shifts of various resonances are summarized in Tables 1 and 2. When 0.20 mol $dm^{-3}$ KSCN was added as a solid (not shown 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

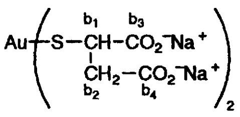
| Species | δ (resonance assignment) |
|---|---|
| $[Au(tm)]_n$ | 47.9 ($a_1$ and $a_2$), 182.2 ($a_3$), 179.6 ($a_4$) |
| $[Au(tm)_2]^-$ | 43.3 ($b_1$), 47.7 ($b_2$), 184.7 ($b_3$), 184.8 ($b_4$) |
| $(tm)_2$ | 54.3 and 54.0 ($d_1$), 41.1 ($d_2$), 180.0 ($d_3$), 179.1 ($d_4$) |
| $[Au(SeCN)(tm)]^-$ | 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$^{-3}$

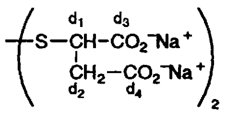
| Fig. | [Au(tm)]$_n$ : KSCN | $a_1$ | $a_2$ | $a_3$ | $a_4$ | SCN$^-$ | $p_1$ | $p_2$ |
|---|---|---|---|---|---|---|---|---|
| 1(*a*) | 0.20:0.00 | 47.9 | 47.9 | 182.2 | 179.6 | — | — | — |
| Not shown | 0.20:0.20 | 47.9 | 47.9 | 182.2 | 179.6 | 133.4 | — | — |
| 1(*b*) | 0.20:0.60 | 47.4 | 47.9 |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



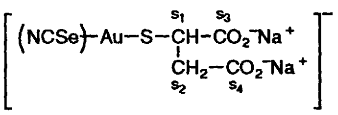
[Au(tm)]$_n$ (tm$^-$ = Thiomalate)



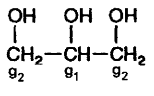
[Au(tm)$_2$]$^-$



(tm)$_2$



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



Glycerol

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]

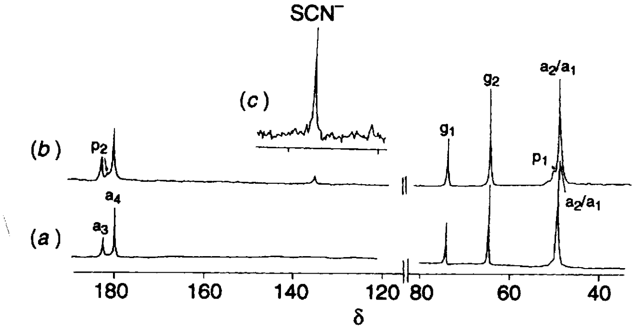


**Fig. 1** The 50 MHz $^1$H noise-decoupled $^{13}$C NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol dm$^{-3}$ [Au(tm)]$_n$, (*b*) 0.20 mol dm$^{-3}$ [Au(tm)]$_n$ : 0.60 mol dm$^{-3}$ KSCN and (*c*) 0.00 mol dm$^{-3}$ [Au(tm)]$_n$ : 0.20 mol dm$^{-3}$ KSCN

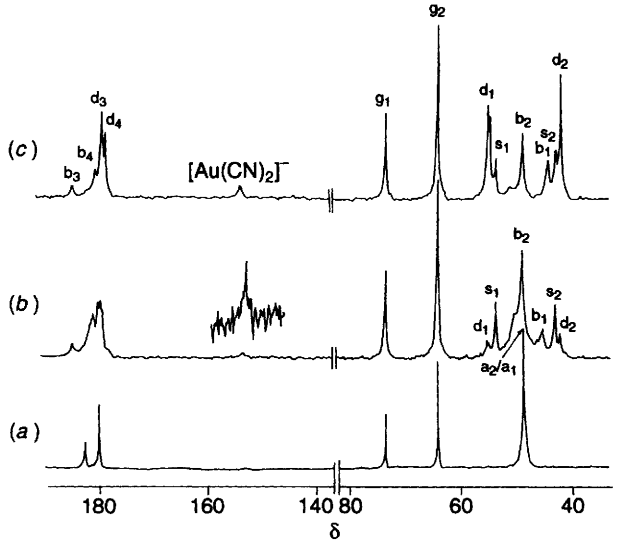


**Fig. 2** The 50 MHz $^1$H noise-decoupled $^{13}$C NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol dm$^{-3}$ [Au(tm)]$_n$, (*b*) 0.20 mol dm$^{-3}$ [Au(tm)]$_n$ : 0.05 mol dm$^{-3}$ KSeCN and (*c*) 0.20 mol dm$^{-3}$ [Au(tm)]$_n$ : 0.10 mol dm$^{-3}$ KSeCN

*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 resona[illegible]re 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).

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

$$\begin{tikzcd} & {[\text{Au(tm)}_2]^- + [\text{Au(SeCN)}_2]^-} \arrow[d] \\ {2[\text{Au(SeCN)(tm)}]^-} \arrow[ur] \arrow[dr] & {[\text{Au(CN)}_2]^- + 2\text{Se}^0} \\ & {(\text{tm})_2 + 2\text{Au}^0 + 2\text{Se}^0 + 2\text{CN}^-} \end{tikzcd} \qquad (2)$$

**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<br>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 | | | | | | | | | | |

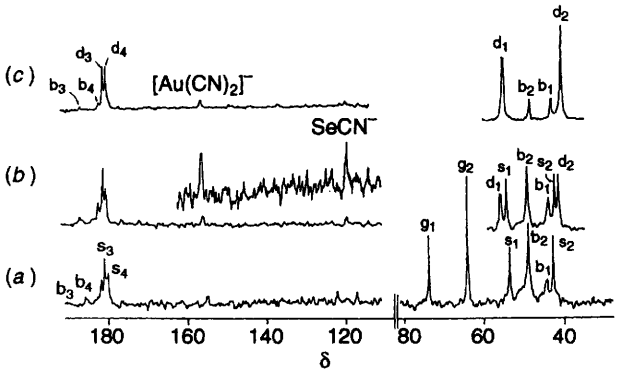


**Fig. 3** The 50 MHz $^1H$ noise-decoupled $^{13}C$ NMR spectra (at pH* 7.40) of 0.20 mol dm$^{-3}$ $[Au(tm)]_n$ : 0.20 mol dm$^{-3}$ KSeCN: (*a*) after 6 h, (*b*) after 12 h and (*c*) after 24 h

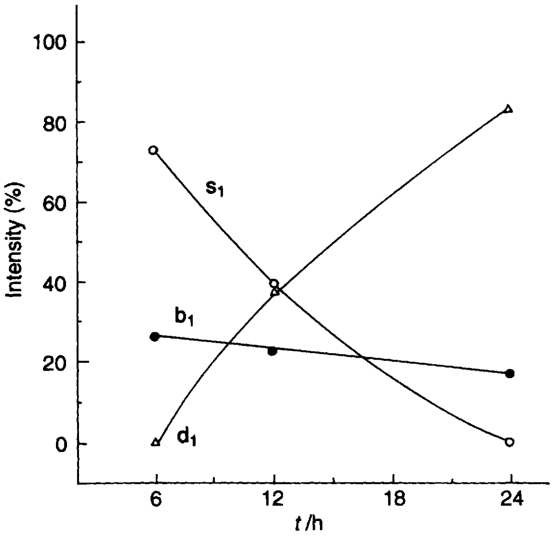


**Fig. 4** The (%) intensity of the CH resonance of tm⁻ as a function of time (for resonance assignment see text)

*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 $D_2O$, 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 $D_2O$ (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 $D_2O$ (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

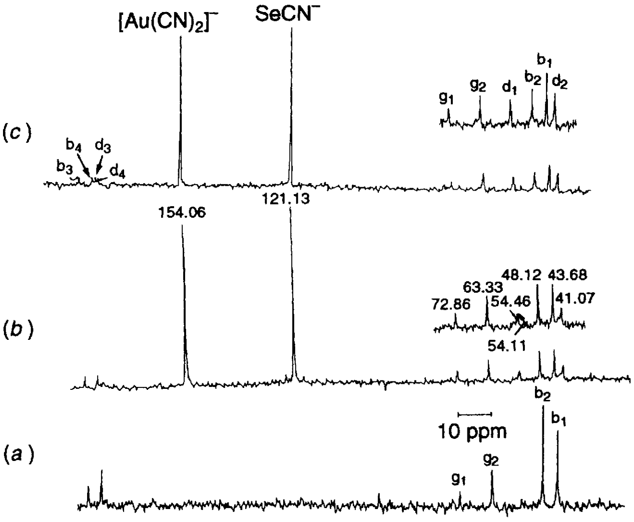


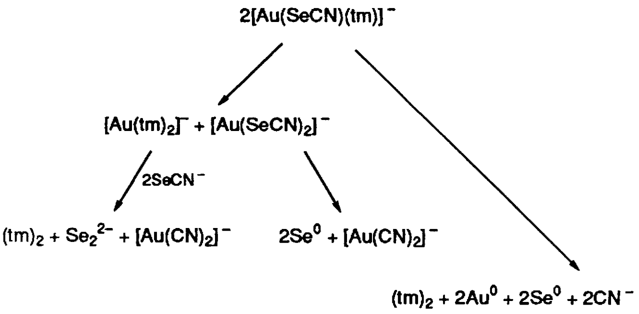
**Fig. 5** The 50 MHz $^1H$ noise-decoupled $^{13}C$ NMR spectra (at pH* 7.40) of: (*a*) 0.20 mol $dm^{-3}$ $[Au(tm)]_n$ : 0.15 mol $dm^{-3}$ Htm; (*b*) as (*a*) + 0.20 mol $dm^{-3}$ $KSe^{13}CN$, spectrum recorded after 12 h, and (*c*) as (*b*) but after 24 h of accumulation

**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<br>54.0 | 41.1 | 180.0 | 179.1 | 155.3 |
| 3(*c*) | 24 | 43.7 | 47.9 | 185.0 | 181.0 | — | — | — | — | 54.3<br>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<br>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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## References

1 P. J. Sadler, *Struct. Bonding* (*Berlin*), 1976, **29**, 171.
2 C. F. Shaw III, *Inorg. Perspect. Biol. Med.*, 1979, **2**, 287.
3 D. H. Brown and W. E. Smith, *Chem. Soc. Rev.*, 1980, **9**, 217.
4 D. H. Brown, G. McKlinley and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1977, 1874.
5 L. F. Larkworthy and D. Sattari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 551.
6 D. T. Hill, B. M. Sutton, A. A. Isab, T. Razi, P. J. Sadler, J. M. Trooster and G. H. M. Callis, *Inorg. Chem.*, 1983, **22**, 2936.
7 A. A. Isab and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1981, 1657.
8 A. A. Isab and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1976, 1051.
9 A. A. Isab and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 135.
10 C. F. Shaw III, J. Eldridge and M. P. Cancaro, *J. Inorg. Biochem.*, 1981, **14**, 267.
11 A. A. Isab, *J. Inorg. Biochem.*, 1987, **30**, 69.
12 A. A. Isab and A. P. Arnold, *J. Coord. Chem.*, 1989, **20**, 95.
13 Y. Park and M. G. Kanatzidis, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 914.
14 M. G. Kanatzidis, *Comments Inorg. Chem.*, 1990, **10**, 161.
15 S. P. Haung and M. G. Kanatzidis, *Inorg. Chem.*, 1991, **30**, 3572.
16 G. G. Graham, T. M. Haavisto, P. J. McNaught, C. D. Browne and G. D. Champion, *J. Rheum.*, 1982, **9**, 527.
17 D. W. James, N. W. Ludvigsen, L. G. Clelend and S. C. Milazzo, *J. Rheum.*, 1982, **9**, 532.
18 G. G. Graham, T. M. Haavisto, H. M. Jones and G. D. Champion, *Biochem. Pharmacol.*, 1984, **33**, 1257.
19 R. D. Hancock, N. P. Finklestein and A. J. Avers, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3747.
20 A. R. Pettitgrew and G. S. Fell, *Clin. Chem.*, 1973, **19**, 466.
21 M. C. Grootveld, M. T. Razi and P. J. Sadler, *Clin. Rheum.*, 1984, **3** (Suppl. 1), 5.
22 V. V. Skopenko, G. V. Tsintsadze and E. I. Ivanova, *Russ. Chem. Rev.*, 1982, **51**, 21.
23 G. G. Graham, J. R. Bales, M. C. Grootveld and P. J. Sadler, *J. Inorg. Biochem.*, 1985, **25**, 163.
24 G. Lewis and C. F. Shaw III, *Inorg. Chem.*, 1986, **25**, 58.
25 A. A. Isab, *J. Inorg. Biochem.*, 1992, **46**, 145.
26 A. A. Isab, I. H. Gazi and A. Al-Arfaj, *J. Chem. Soc., Dalton Trans.*, 1993, 841.
27 A. L. Hormann-Arendt and C. F. Shaw III, *Inorg. Chem.*, 1990, **29**, 4683.
28 A. A. Isab, A. L. Hormann, M. T. Coffer and C. F. Shaw III, *J. Am. Chem. Soc.*, 1988, **110**, 3278.
29 A. A. Isab, I. H. Gazi, M. I. M. Wazeer and H. Perzanowski, *J. Inorg. Biochem.*, 1993, **50**, 299.
30 A. A. Isab, *Transition Met. Chem.*, 1994, **19**, 495.
31 A. A. Isab, A. R. Al-Arfaj and M. N. Akhtar, *J. Coord. Chem.*, 1994, **33**, 287.

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