

# FORMATION AND REACTIVITY OF $[\text{Au}^{(13}\text{CN})_4^{(-)}]$ , $[\text{Au}^{(13}\text{CN})_3\text{Cl}^{(-)}]$ AND $[\text{Au}^{(13}\text{CN})_3(\text{SR})^{(-)}]$ STUDIED BY $^{13}\text{C}$ NMR SPECTROSCOPY

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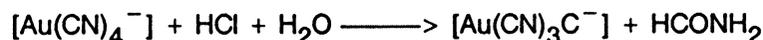
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$\text{Au}(\text{CN})_2^-$  is generated from gold(I) complexes and thiocyanate during the oxidative burst.<sup>1</sup>  $\text{Au}(\text{CN})_2^-$  can be also oxidized to gold(III) under similar conditions.<sup>2</sup> Thus, it is of interest to examine the chemistry of  $\text{Au}(\text{CN})_4^-$ , the gold(III) complex of cyanide.

$\text{Au}^{(13}\text{CN})_4^-$  can be generated by reacting  $\text{AuCl}_4^-$  (yellow,  $\lambda_{\text{max}} = 316 \text{ nm}$ ) with 4 equiv. of  $^{13}\text{CN}^-$  producing a colourless solution ( $\lambda_{\text{max}} = <200 \text{ nm}$ ). This species is characterized by a single  $^{13}\text{C}$  NMR resonance at 104.6 ppm. In HCl solutions up to 5 M, there is no initial displacement of  $^{13}\text{CN}$  to form a mixed ligand chloride solution, indicating that the equilibrium lies far to the left even under drastic conditions:



Upon standing 12-24 hr in 5 or 10 M HCl, however, slow hydrolysis of cyanide to formamide ( $\text{HCONH}_2$ ) drives the formation of  $[\text{Au}(\text{CN})_3\text{Cl}^-]$ :



$[\text{Au}(\text{CN})_3\text{Cl}^-]$  which is square planar gives a doublet ( $\delta = 111.1 \text{ ppm}$ ) and a triplet ( $\delta = 94.7 \text{ ppm}$ ), 2:1 ratio, due to  $^2J_{^{13}\text{C}^{13}\text{C}}$  coupling of the cyanides trans and cis to the chlorides.

We also generated  $[\text{Au}^{(13}\text{CN})(\text{SR})]^-$  (where  $\text{SR}^- = \text{glutathione, N-acetyl-L-cysteine}$ ) by adding one equivalent of thiol in phosphate buffer. These complexes undergo a slow redox reaction to form dicyanogold(I) and RSSR:



For thionitrobenzoate (TNB) and cysteine the redox reactions apparently proceed faster, so that just the disulfide and gold(I) cyanide are observed, not the intermediate complex. UV-visible titrations for the reaction of  $[\text{Au}(\text{CN})_4^-]$  with excess TNB establish the stoichiometry:



These results suggest that the formation of  $[\text{Au}(\text{CN})_4^-]$  can lead to thiol oxidation and re-reduction of gold(I). Thus, a gold(I)/gold(III) redox cycle may be established *in vivo* even under conditions where generation of gold cyanides from  $\text{SCN}^-$  during the oxidative burst prevails.

1. G.Graham *et al.*, *Biochem. Pharmacol.*, 39, 1687-1695 (1990).
2. C. F. Shaw III *et al.*, Proc. 3rd Intern. Conf. Gold Silver Med., *Metal Based Drugs*, this issue (1994).