

EFFECT OF ENVIRONMENT ON DICYANOAUROATE IONS – CRYSTALLINE, FROZEN SOLUTION AND CARBON-ADSORBED SPECIES

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^{197}Au Mössbauer spectra of crystalline samples of the dicyanoaurates of Na^+ , K^+ , $\text{Ca}^{2+}/\text{Na}^+$ and Gd^{3+} show that the spectral parameters for the first three are all similar to each other and to a sample of frozen aqueous solution of $\text{KAu}(\text{CN})_2$. Spectra of activated carbon samples treated with $\text{NaAu}(\text{CN})_2$ or $\text{KAu}(\text{CN})_2$ solution increased in both isomer shift and quadrupole splitting accompanied by a removal of Gol'danskii-Karyagin effect asymmetry. Drying the samples produced a small reduction in the isomer shift and quadrupole splitting. The results show that the gold atoms are not closely associated with either the cations or with water molecules in the samples. Interpretations are given in terms of the bonding of the Au ion to the substrate.

1. Introduction

The carbon-in-pulp (C-I-P) process has been used successfully for many years for the extraction of small amounts of gold (2 mg.l^{-1}) from cyanide pulps. In this process milled ore is agitated with activated carbon, which acts as a collector, in a dilute alkaline cyanide solution, buffered to pH 10.5, in the presence of air and passed through columns containing activated carbon. The adsorbed gold species are subsequently removed by treatment with solutions such as hot NaOH/NaCN or organic solvents e.g. acetonitrile [1]. An improved understanding of the physical and chemical processes involved may suggest methods for improving the efficiency of one or more of these stages. However the industrial process uses Na^+ (and potentially Ca^{2+} ions which are present in the pH buffering agent $\text{Ca}(\text{OH})_2$) as the counter ions to the $\text{Au}(\text{CN})_2^-$ and interpretation of our preliminary results on the system [2,3] have been hampered by a lack of literature values for $\text{NaAu}(\text{CN})_2$ and $\text{Ca}\{\text{Au}(\text{CN})_2\}_2$.

The current understanding of the adsorption of gold onto activated carbon from dicyanoaurate solution is based on several different types of experiments, the conclusions of which are not all in agreement. The wet chemical experiments of Tsuchida and Muir [4,5] were interpreted in terms of an oxidative adsorption mechanism of $\text{Au}(\text{CN})_2^-$ with the liberation of OH^- during which the potential of the carbon drops. No K^+ is adsorbed at low concentrations while the ratio of $\text{Au}(\text{CN})_2^-:\text{K}^+$ is approximately 2:1 at the higher concentrations. The process is not a simple ion exchange and neutral species are suggested for subsequent partial oxidative decomposition of the $\text{Au}(\text{CN})_2^-$ species.

X-ray photoelectron spectroscopy (XPS) measurements by McDougall et al. [6] were interpreted as a partial reduction of the dicyanoaurate ion with the final oxidation number of the gold being 0.3. Following further studies with E.S.R. spectroscopy McDougall et al. [7] have postulated that the adsorption mechanism may involve a charge transfer from the condensed aromatic structure on the carbon to vacant orbitals in the gold complex.

Subsequent XPS measurements by Klauber [8] suggested that the bonding of the $\text{Au}(\text{CN})_2^-$ was via the transfer of 0.3 to 0.5 of an electron from the graphite π electrons to the gold and that the nitrogen atoms were not involved in the bonding.

Mössbauer measurements by our group [2,3] have shown that the adsorbed gold species is $\text{Au}(\text{CN})_2^-$ and no evidence has been obtained for other species at $\text{pH} > 10$. The bonding was postulated to be principally at the terminal nitrogen atoms.

McDougall et al. [7] also observed an approximately tenfold increase in the adsorption of the dicyanoaurate when the carbon is activated above 850°C which coincides with our observation [9] of a large increase in iron adsorption after activation at the same temperature.

There are many variables in the cyanide-gold-carbon system which may contribute to differences in the results, the interpretation of the bonding of the groups and their applicability to the industrial process. These include the role of different carbons, different and mixed cations, concentration dependence, pH dependence and differences between laboratory and plant conditions. In this paper we provide reference data for crystalline dicyanoaurates other than the previously measured potassium salt and then, with measurements of a frozen solution of $\text{KAu}(\text{CN})_2$ and wet and dried dicyanoaurate-loaded carbons originating from laboratory and plant processes, go on to draw conclusions on the bonding of the gold atom and its proximity to cations and water molecules.

2. Experimental

2.1. Samples

(a) Crystalline samples

The $\text{KAu}(\text{CN})_2$ starting material was commercial powder from Johnson-Matthey. The $\text{NaAu}(\text{CN})_2$ was prepared from AuCN and NaCN by the method outlined by Penneman and Staritzky [10]. The preparation of $\text{Ca}\{\text{Au}(\text{CN})_2\}_2$ does not appear to be described in the literature. An expected mixed $\text{Ca}_x\text{Na}_{2-2x}$ salt was prepared by the method of Barbieri [11] using $\text{NaAu}(\text{CN})_2$ and $\text{Ca}(\text{NO}_3)_2$. The reason for the mixed salt is that $\text{Ca}\{\text{Au}(\text{CN})_2\}_2$ is only stable in the presence of some other cation. The $\text{Gd}\{\text{Au}(\text{CN})_2\}_3$ sample was prepared in a similar fashion by dissolving Gd metal in dilute HNO_3 and mixing with $\text{KAu}(\text{CN})_2$. Atomic absorption analysis of the crystals did not detect any trace of potassium.

In order to reduce the possibility of precipitation of $\text{KAu}(\text{CN})_2$ from solution during freezing, a 0.55 M solution was dropped from a plain pipette into a liquid nitrogen cooled teflon absorber holder and maintained at 77K before taking the Mössbauer spectrum.

(b) Activated Carbon

Coconut char granules (Kintal, Japan) were initially crushed to facilitate making into absorbers for Mössbauer spectroscopy and to obtain a higher gold loading. It is not expected that this will affect the validity of the results. A decolourizing charcoal powder (AJAX Chemicals, U.S.A.) was already a fine powder and so was not crushed further. A new laboratory prepared activated carbon was made at the Gippsland Institute of Advanced Education from jarrah char.

(c) Laboratory prepared carbon samples

These samples were prepared by placing approximately 6 g of the coconut char into a 100 ml aqueous solution of 3 g of each of the K and Na dicyanoaurate salts, maintained

at pH 10.5 with the respective cation hydroxide as a buffering agent. After standing for 24 hours, the carbon was filtered from the solution but was not washed or rinsed.

(d) Gold Mine carbon samples

Two industrial samples were obtained from NaCN solution leaching a calcined gold concentrate at pH 10.5, buffered with lime. In the first, from Lakeview and Star Mines Pty. Ltd., Kalgoorlie, Western Australia, Haycarb YAO activated carbon was used and the sample was already dry when received. The second sample from Western Mining Corp. Pty. Ltd., Stawell, Victoria, was adsorbed onto the jarrah char activated carbon and was wet when received. The gold concentrations on the samples were approximately 1 wt.% and approximately 1.5 wt.% respectively.

The laboratory prepared carbon samples and the industrial sample from Stawell were run while still wet. The laboratory prepared samples were later re-run after sitting for 8 months in storage at 6°C. The NaAu(CN)₂ laboratory prepared sample was later dried at 80°C for 24 hours.

2.2. ¹⁹⁷Au Mössbauer Measurements

The source was natural platinum for the earlier samples and isotopically enriched (96%) ¹⁹⁶Pt for the majority of the experiments. Each source was irradiated for 12 hours at the A.N.S.T.O. HIFAR reactor in a neutron flux of $5 \times 10^{13} \text{ cm}^{-2}\text{sec}^{-1}$. All of the measurements were taken with both the source and absorber cooled to 4.2 K in a liquid helium cryostat and isomer shift values are given relative to Au metal.

For the crystalline and frozen samples, absorbers containing approximately 200 mg.cm⁻² of gold were used. It has been shown [12, p.610] that the recoilless fraction for many Au(I) compounds with a molecular mass in the range 300–700 is approximately 0.03–0.04. From this we can expect the effective absorber thickness, T_a , of the crystalline samples to be of the order of 1.0–1.5. Approximately 4–6 g of each carbon sample was placed in a 12 mm diameter aluminium tube. The amount of gold on the carbon was not determined but it is expected to be in the vicinity of 300 mg.cm⁻². The problems associated with thickness effects were obviously negligible as the measured halfwidths of the absorption dips were within 15% of the natural linewidth.

The data could in general be adequately fitted with a lorentzian doublet. However, for the non-carbon samples, the spectra displayed some asymmetry in the intensity of the dips. These were fitted with 2 lorentzian singlets with independent intensities but the values of the halfwidths were constrained to be the same. The values given for the asymmetry are calculated from the ratio of intensities, right hand peak/left hand peak.

3. Results

All of the ¹⁹⁷Au Mössbauer spectra for the dicyanoaurate complexes in the various forms studied in this work are essentially the same in appearance. Figure 1 shows a typical spectrum for the Au(CN)₂⁻ anion on activated carbon as well as that for the frozen KAu(CN)₂ solution.

Spectra of the crystalline sodium, potassium and calcium/sodium salts all had very similar parameters while the gadolinium salt had a markedly smaller isomer shift and quadrupole splitting (see Table 1 and Figure 2). All exhibited an asymmetry in the line intensities due to a contribution of the Gol'danskii-Karyagin effect and texture as investigated by Prosser

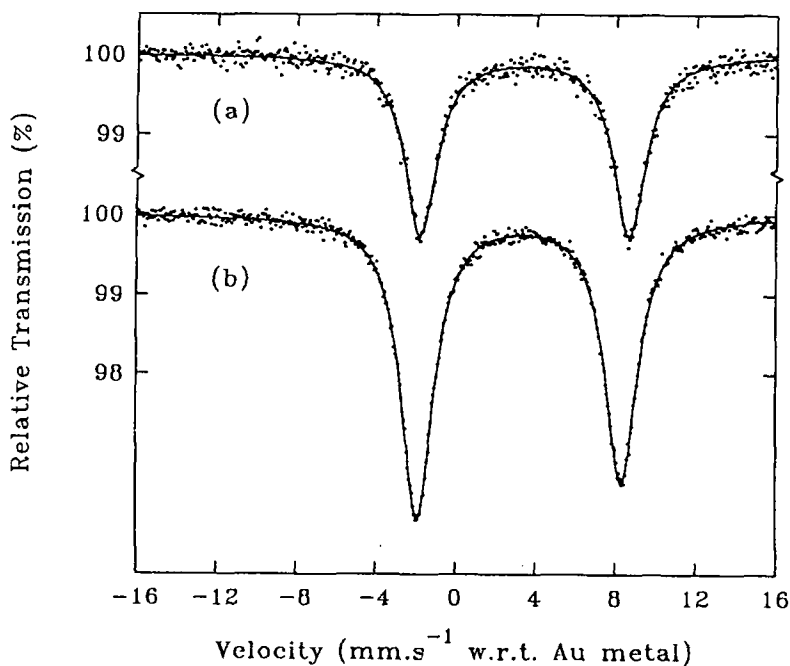


Figure 1 :

¹⁹⁷Au Mössbauer spectra characteristic of the $\text{Au}(\text{CN})_2^-$ anion.

(a) Activated carbon sample taken from $\text{KAu}(\text{CN})_2$ solution.

(b) Frozen solution of $\text{KAu}(\text{CN})_2$ in double-distilled water.

et al. [13,14]. This asymmetry varied between samples as seen in Table 1, and also changed with time but no attempt has been made to evaluate the relative effects of the two causes.

The parameters for the frozen solution are very close to those of crystalline $\text{KAu}(\text{CN})_2$, however the asymmetry is much greater than for the other samples and this should be sufficient to dispel doubts that the sample may have crystallized rather than frozen.

The spectral parameters for the carbon samples are very similar to each other (Table 2, Figure 2) but show an increase in both isomer shift and quadrupole splitting from the crystalline set. A more remarkable effect was the complete absence of any line asymmetry in the spectra of these samples. Allowing the samples to age in their absorber holder at constant water content, resulted in a reduction of approximately a factor of two in the recoilless fraction for both the sodium and potassium samples. Drying resulted in a further factor of two decrease in the recoilless fraction, as well as a small reduction in both the isomer shift and the quadrupole splitting.

Spectral parameters of the industrial carbon samples were identical to those of the laboratory samples, but it was not possible to compare the recoilless fraction with any accuracy. Figure 2 shows all of the above results in graphical form to highlight the linear correlation

Table 1 :

Isomer shift, quadrupole splittings, asymmetry and linewidth (FWHM) for the starting materials used in this work. The errors given in the parentheses are 90% confidence limits.

Cation	IS mm s ⁻¹	QS mm s ⁻¹	asymm.	Γ mm s ⁻¹
K ⁺	4.41(5)	10.13(5)	0.99(3)	1.92(4)
Na ⁺	4.42(5)	9.98(5)	0.88(2)	2.02(4)
Ca ²⁺ /Na ⁺	4.45(7)	10.04(9)	0.87(6)	2.00(10)
Gd ³⁺	4.15(5)	9.45(5)	0.97(2)	2.18(4)
K ⁺ (soln.)	4.45(5)	10.21(5)	0.88(2)	1.96(4)

Table 2 :

Isomer shift and quadrupole splittings for the Au(CN)₂⁻ anion adsorbed on activated carbon but with different cations in the initial solutions.

Cation		IS mm s ⁻¹	QS mm s ⁻¹	Γ mm s ⁻¹
<i>Lab</i>				
	K ⁺ wet	4.70(5)	10.50(5)	1.96(6)
	K ⁺ wet ^a	4.61(6)	10.25(7)	2.02(8)
	Na ⁺ wet	4.71(6)	10.47(7)	1.90(9)
	Na ⁺ wet ^a	4.68(7)	10.47(9)	1.92(12)
	Na ⁺ dry	4.69(8)	10.37(10)	2.00(14)
<i>Industrial</i>				
Kalgoorlie	Ca ²⁺ /Na ⁺ dry	4.71(18)	10.42(31)	2.24(46)
Stawell	Ca ²⁺ /Na ⁺ wet	4.71(8)	10.45(10)	2.02(16)

^a Spectrum taken 8 months after preceding run.

known to exist between the quadrupole splitting and isomer shift for most gold compounds.

4. Interpretations and Conclusions

The similarity of the spectral parameters within the Na, K, Ca crystalline group and within the carbon samples shows that the cations are not in the proximity of the gold atom, a fact already known from x-ray data for the KAu(CN)₂ structure. The slope of the fit to figure 2 is 1.7 and its excellent linearity indicates [15,12] that there is no change in 6s-6p_z hybridization in the samples studied. Further discussion of this aspect will be the subject of another paper.

The isomer shift change of 0.29 mms⁻¹ can be interpreted [15,12] as an increase in 6s electron density of 0.036 electrons on bonding onto the carbon. The changes in the quadrupole splitting of 0.37 mms⁻¹ (K sample) and 0.49 mms⁻¹ (Na sample) could be interpreted as an increase of 0.02 6p_z electrons. An alternate possibility is the filling of 5d holes left by the gold electrons transferring to the π*-antibonding orbital with the cyanide. Such a filling will

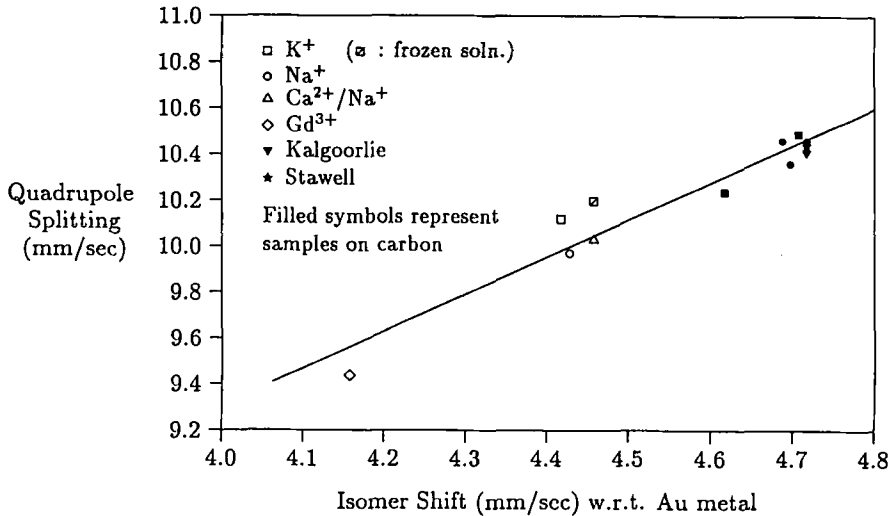


Figure 2 :

Correlation diagram of quadrupole splitting vs. isomer shift for the dicyanoaurate samples.

reduce the positive electric field gradient contribution from the $5d$ shell and hence increase the (negative) electric field gradient due principally to the $6p_z$ electrons. However such a change will also increase the shielding of the $6s$ electrons making the previous estimate of a 0.036 $6s$ electron transfer a slight underestimate.

The removal of the line asymmetry caused by bonding onto the carbon also provides evidence for some of the bonding to be at the gold site since this will reduce the asymmetry in the r.m.s. amplitude of vibration of the linear $(N-C-Au-C-N)^-$ molecule. However our conceptual model is that the principal bonding is at the terminal nitrogens of the $Au(CN)_2^-$ complex, in disagreement with the conclusions from [8]. These conclusions do not appear to be compatible with the small electron transfer to the gold indicated by our results and the experiments of Tsuchida and Muir [4,5], which show that $Au(CN)_2^-$ adsorption is as an anion with liberation of OH^- and a net resulting electron transfer to the substrate.

The change in the recoilless fraction on drying cannot be interpreted in terms of the relatively small mass change involved in separating a small number of water molecules from the heavy $Au(CN)_2^-$ ion. In the work of McDougall et al. [16] water molecules were found to bond at the nitrogen atoms. Removal of water molecules would result in some redistribution of electrons along the bonding chain and hence alter the bonding as seen at the gold atom. The very large Gol'danskii-Karyagin effect seen in the frozen solution is consistent with a hydrogen in a water molecule being bonded to a negatively charged nitrogen [6]. There is no bonding at the gold atom, allowing it an even greater freedom for sideways vibration than in the solid dicyanoaurates.

The results of ^{197}Au Mössbauer spectra presented here are not strongly sensitive to either the cation or to the presence of water molecules, suggesting that both species are

well removed from the gold atom. It is expected that current work on polymerized gold cyanide samples and deoxygenated activated carbons will allow more detailed conclusions on the bonding of the $\text{Au}(\text{CN})_2^-$ ions to carbon substrates.

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