The Redox Behaviour of Square-planar *trans*-Dicyanodihalogenoaurate(III) Complexes in Acetonitrile

Jale Hacaloğlu, Namik K. Tunali,* and Ural Akbulut
Department of Chemistry, Middle East Technical University, Ankara, Turkey

The redox behaviour of *trans*-$[\mathrm{NBu}^n_4][\mathrm{Au(CN)_2X_2}]$ (X = Cl, Br, or I) and $[\mathrm{NBu}^n_4][\mathrm{Au(CN)_2}]$ have been investigated in acetonitrile solution. The effect of σ and π donor halides and π acceptor cyanide on the redox behaviour have also been studied. Intermediates are observed in the redox reactions of these systems.

The therapeutic [1] and catalytic [2,3] action of gold may be attributed to the unsaturation of its complexes with respect to co-ordination number. Gold in its +1 oxidation state forms two-co-ordinate linear complexes while gold(III) forms four-co-ordinate square-planar complexes. The change in energy of the *d* orbitals depends on the nature of the ligands.[4] The presence of π acceptor ligands such as cyanides stabilizes the d_{xy} orbital of π symmetry, and increases the energy splitting between the highest occupied and lowest unoccupied orbitals. Halide ions are poor σ donors but good π donors. Their presence has a large destabilizing effect on the d_{xy} orbital, while their effect on $d_{x^2-y^2}$ is small.[5,6] Therefore the energy splitting between these orbitals is reduced. In the mixed complexes of cyanides and halides a behaviour in between is expected.[6]

Experimental

Preparation of Compounds.—The complexes $[\mathrm{NBu}^n_4][\mathrm{Au(CN)_2}]$,[6,7] *trans*-$[\mathrm{NBu}^n_4][\mathrm{Au(CN)_2X_2}]$ [6,8] (X = Cl, Br, or I), and $[\mathrm{NBu}^n_4][\mathrm{BF_4}]$ [9] were prepared according to literature methods.

Measurements.—All solutions for u.v. spectra were prepared with spectral grade $\mathrm{CH_3CN}$. Measurements were made on a Cary 17D spectrophotometer. I.r. measurements were made on a Perkin-Elmer 421 spectrometer as Nujol mulls.

Cyclic voltammograms (c.v.) were obtained by using a Tacussel Electronique Potentiostat type PRT 30-0.1 and a SeSa-1 function generator. The measurements were made in acetonitrile which was purified according to the literature method,[10] and stored over molecular sieves (Linde A4) before use.

Coulometric analyses were carried out with the same system used for c.v. but instead of using a platinum wire a platinum plate electrode was employed as the working electrode. Nitrogen gas was allowed to pass through the solution during electrolysis.

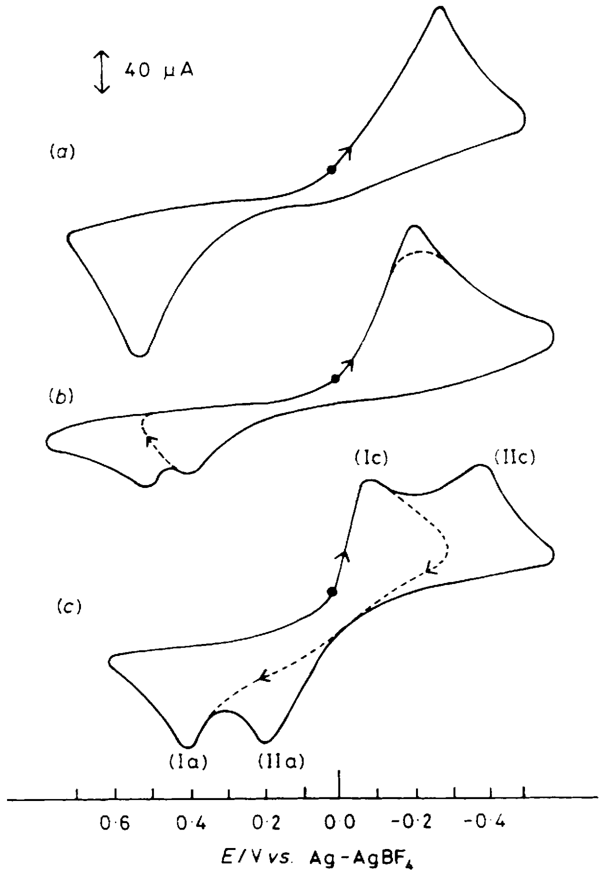


Figure. Cyclic voltammograms of *trans*-$[\mathrm{NBu}^n_4][\mathrm{Au(CN)_2X_2}]$ in $\mathrm{CH_3CN}$; (*a*) X = Cl, (*b*) X = Br, (*c*) X = I. Scan rate was 200 mV $\mathrm{s^{-1}}$

Discussion

Cyclic Voltammetry.—The cyclic voltammogram of $[\mathrm{Au(CN)_2Cl_2}]^-$ shows one reduction and one oxidation peak at −0.30 and 0.50 V, respectively. One reduction peak at −0.20 V and two oxidation peaks at 0.40 and 0.50 V are present in the c.v. of $[\mathrm{Au(CN)_2Br_2}]^-$. In the case of $[\mathrm{Au(CN)_2I_2}]^-$ there are two reduction peaks (−0.08 and −0.40 V) and two oxidation peaks (0.20 and 0.40 V) (Figure).

When the anodic scans were first obtained no oxidation peak (for the chloro-complex) or very weak oxidation peaks (for the bromo- and iodo-complexes) were observed. These observations indicate that the anodic peaks are due to the oxidation products of the reduced forms of the original complexes. Clipping at 0.40 V decreases the intensity of the reduction peak at −0.20 V in the case of the bromo-complex and indicates that the oxidation peaks are related to the reduction peak [Figure (*b*)]. Similarly related peaks of the iodo-complex are shown by Roman numerals in Figure (*c*).

The separations between the related peaks are 408, 600, and 800 mV where X = $\mathrm{I^-}$, $\mathrm{Br^-}$, or $\mathrm{Cl^-}$, respectively. This indicates that the redox reactions of these complexes are all irreversible. Furthermore peak separation is a measure of the rate of redox reaction. When the separation is large the reaction is expected to be slow. Therefore it can be concluded that the presence of halogens in these complexes increases the rate of the redox reaction in the order $Cl^- < Br^- < I^-$.

Electron-donating groups cause easier oxidation and more difficult reduction, whereas electron-withdrawing groups have the opposite effect. Higher oxidation states of metals are stabilized by electron-donating groups while the lower oxidation states are stabilized by electron-withdrawing groups. The cyclic voltammogram of $[Au(CN)_2]^-$ does not show any peak within the solvent-electrolyte range (−2.40 to 2.40 V). This is in agreement with the above statement concerning electron-withdrawing groups such as CN^-, and makes oxidation of the complex possible only at very high anodic potentials. Halide ions are known to be σ and π donors. Electron-donating power of halides follows the order $Cl^- < Br^- < I^-$. According to the above generalization it is expected that for the complexes containing halides there should be a negative shift in both reduction and oxidation potentials (being greatest in the iodo-complex). The cyclic voltammograms show that this tendency is obeyed in the oxidation potentials, but the reduction potentials follow the opposite trend (Table 1). This may be explained by the observation that the force constants of Au–X, Au–C, and C–N become smaller on going from the chloro- to the iodo-complex.[8] Since the redox reactions of these complexes involve the breakage or formation of Au–X bonds it can be expected that both reduction and oxidation are easier in weakly bonded complexes.

Table 1. Redox data for *trans*-$[NBu^n_4][Au(CN)_2X_2]$ (X = Cl, Br, or I) at a platinum electrode in CH_3CN at room temperature (E/V *vs.* Ag–$AgBF_4$)

	Reduction		Oxidation	
	E_p/V	n	E_p/V	n
$[Au(CN)_2Cl_2]^-$	−0.30	2	0.50	2
$[Au(CN)_2Br_2]^-$	−0.20	2	0.40	1
			0.50	1
$[Au(CN)_2I_2]^-$	−0.08	1	0.20	1
	−0.40	1	0.40	1

Controlled Potential Electrolysis.—These experiments were carried out to determine the number of electrons transferred at each peak and to prepare products at these peak potentials, for their identification. In the chloro-complex the number of electrons transferred at each peak is calculated to be two (Table 1). In the case of the bromo-complex the reduction peak at −0.20 V corresponds to a two-electron transfer

Table 2. Electronic spectral data for acetonitrile solutions of *trans*-$[NBu^n_4][Au(CN)_2X_2]$ (X = Cl, Br, or I), their oxidation and reduction products, and $[NBu^n_4][Au(CN)_2]$ in acetonitrile

Parent complex $\nu/\mu m^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)	Assignment[a]	Reduction product $\nu/\mu m^{-1}$		Oxidation product of the reduced complex $\nu/\mu m^{-1}$	
(*a*) $[Au(CN)_2Cl_2]^-$					
		at −0.30 V		at 0.50 V	
3.42 (1 125.6)	L → M	4.18		3.45	
4.55 (21 842.5)	L → M	4.22		4.65	
4.90 (13 851.8)	M → L	4.41		4.95	
		4.55			
		4.70			
		4.88			
(*b*) $[Au(CN)_2Br_2]^-$					
		at −0.20 V		at 0.40 V	at 0.50 V
2.82[b] (632.5)	L → M	4.19		4.17	2.83
3.13 (857.5)	L → M	4.24		4.26	3.33
4.20 (28 486.5)	L → M	4.41		4.41	4.26
4.81 (13 875.3)	M → L	4.55		4.59	4.88
4.95 (13 348.2)	M → L	4.70		4.72	4.95
		4.88		4.88	
(*c*) $[Au(CN)_2I_2]^-$					
		at −0.08 V	at −0.40 V	at 0.20 V[d]	at 0.40 V[c]
2.76 (4 685.8)	L → M	2.78	4.17	2.78	
3.65 (38 575.2)	L → M	3.53	4.26	3.65	2.78
4.26 (20 486.2)	M → L	4.22	4.41	4.26	3.70
4.66 (23 875.2)		4.55	4.57	4.41	4.35
4.92 (34 348.2)	M → L	4.95	4.72	4.72	4.72
			4.89	4.91	4.95
(*d*) $[Au(CN)_2]^-$					
4.18 (4 519.7)	M → L				
4.33 (3 389.8)	M → L				
4.42 (2 604.7)	M → L				
4.58[b] (2 259.8)	M → L				
4.72 (11 299.4)	M → L				
4.88 (16 271.1)	M → L				

[a] $[Au(CN)_2X_2]^-$ were assigned using ref. 6 and $[Au(CN)_2]^-$ by using ref. 7*a*. [b] Shoulder. [c] Oxidation product of the reduced complex at −0.08 V. [d] Oxidation product of the reduced complex at −0.40 V.

process, whereas the oxidation peaks (0.40, 0.50 V) correspond to two one-electron transfer processes. All the reduction (−0.08 and −0.40 V) and oxidation peaks (0.20 and 0.40 V) in the c.v. of the iodo-complex correspond to one-electron transfer processes.

U.v. Spectra.—The electronic spectra of dicyanodihalogeno-complexes of gold show a shift towards lower energy when the halogen changes from chlorine to iodine.[6] The tetrahalogeno-complex has L ⟶ M charge-transfer transitions while the tetracyano-complex has M ⟶ L charge-transfer transitions.[4,5] As expected dicyanodihalogeno-complexes have both L ⟶ M and M ⟶ L charge-transfer transitions.[6] U.v. spectra of the samples, obtained by electrolysis at each peak, have been recorded for identification purposes. All relevant data are summarized in Table 2.

The u.v. spectra of the reduction products at the lowest peak potentials were compared with those of the corresponding dihalogeno- and dicyano-complexes. It was observed that the spectra of the reduced complexes were similar to that of $[Au(CN)_2]^-$ but not to those of the corresponding $[AuX_2]^-$.[11] The spectra at the highest peak potentials resemble those of the corresponding $[Au(CN)_2X_2]^-$. The spectra of the products at the peaks in between the above peak potentials resemble either those of the initial species or both of those of the initial and final species $\{[Au(CN)_2I_2]^-\}$.

I.r. Spectra.—The vibrational spectra of the products obtained at various peak potentials agree with the corresponding u.v. spectra regarding the identification of the species. Comparison of the spectra shows that the asymmetric CN stretching vibration signal of linear $[Au(CN)_2]^-$ appears at the lowest frequency while that of the square-planar $[Au(CN)_4]^-$ is at the highest frequency. The corresponding signals of dicyanodihalogenoaurate(III) complexes lie in between these values.

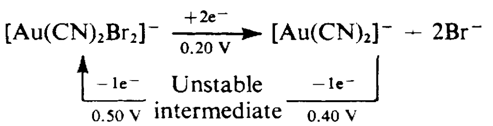
Halide ions are known to be electron donors amongst which iodide is the most powerful donor. Their presence in the co-ordination sphere increases the π interaction between metal and carbon and decreases the π interaction between carbon and nitrogen.[12,13] Because of this the iodo-complex has the lowest stretching frequency among dicyanodihalogeno-complexes. These observations are in agreement with the studies on force constants of Au–C and C–N bonds for dicyanodihalogeno-complexes.[5]

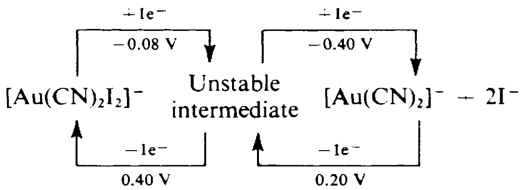
Conclusions

In the light of the present investigation, the following mechanisms for the redox reactions of *trans*-$[NBu^n_4][Au(CN)_2X_2]$ (X = Cl, Br, or I) may be proposed for acetonitrile solutions.

The presence of one reduction and one oxidation peak in the cyclic voltammogram of $[Au(CN)_2Cl_2]^-$ may lead one to consider that the reaction occurs without a detectable intermediate. For $[Au(CN)_2Br_2]^-$ the existence of one reduction

$$[Au(CN)_2Cl_2]^- \xrightarrow[-0.30\ V]{+2e^-} [Au(CN)_2]^- + 2Cl^- \xrightarrow[0.50\ V]{-2e^-} [Au(CN)_2Cl_2]^-$$





but two oxidation peaks may indicate an intermediate with two transition states with a considerable energy difference. Two reduction and two oxidation peaks in the voltammogram of $[Au(CN)_2I_2]^-$ may suggest the existence of a relatively more stable intermediate.

Acknowledgements

We wish to thank Dr. H. İşçi for helpful discussions and for the preparation of *trans*-$[NBu^n_4][Au(CN)_2X_2]$ (X = Br or I). We are also grateful to the British Council for the supply of chemicals used in this work.

References

1 P. J. Sadler, *Gold Bull.*, 1976, **9**, 110.
2 P. A. Sermon, *Gold Bull.*, 1976, **9**, 129.
3 J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, 1965, **87**, 4008.
4 W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 5721.
5 A. J. McCaffery, P. N. Schatz, and P. J. Stefens, *J. Am. Chem. Soc.*, 1968, **90**, 5730.
6 H. İşçi and W. R. Mason, *Inorg. Chem.*, 1983, **22**, 2266.
7 (*a*) W. R. Mason, *J. Am. Chem. Soc.*, 1973, **95**, 3573; (*b*) O. Glemser and H. Sauer, 'Handbook of Preparative Inorganic Chemistry,' 2nd edn., ed. G. Brauer, Academic Press, New York, 1965, vol. 2, p. 1065.
8 L. H. Jones, *Inorg. Chem.*, 1964, **3**, 1581.
9 U. Akbulut, R. C. Birke, and J. E. Fernandez, *Macromol. Chem.*, 1978, **179**, 2507.
10 U. Akbulut, Ph.D. Thesis, University of South Florida, 1973.
11 M. K. Koutek and W. R. Mason, *Inorg. Chem.*, 1980, **19**, 648.
12 J. M. Smith, L. H. Jones, I. K. Kressin, and R. A. Penneman, *Inorg. Chem.*, 1965, **1**, 369.
13 L. H. Jones, *Inorg. Chem.*, 1963, **2**, 777.

Received 3rd May 1983; Paper 3/696