

Spectral and photochemical characterization of the chlorodicyanocuprate(I) complex in aqueous solution

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Abstract

Absorption and emission spectra of aqueous solutions of $\text{Cu}(\text{CN})_2^-$ in which the chloride concentration was varied from 0.2 to 5 M were investigated. Spectral information indicates the formation of the $\text{Cu}(\text{CN})_2\text{Cl}^{2-}$ complex. The value of the equilibrium constant for the reaction $\text{Cu}(\text{CN})_2^- + \text{Cl}^- = \text{Cu}(\text{CN})_2\text{Cl}^{2-}$ is 0.70 ± 0.12 M at 5 M ionic strength. Excitation of the copper(I) complex in neutral aqueous solution containing 5 M chloride ion at room temperature results in luminescence emission centered at 475 nm with a quantum yield of $6.9 \pm 1.5 \times 10^{-4}$ and a lifetime of 97.5 ± 5.0 ns. Laser flash experiments (excitation at 266 nm) indicated the formation of hydrated electrons. The quantum yield of this process for the mixed ligand complex determined by continuous irradiation at 254 nm using electron scavengers (N_2O and NO_3^-) is 0.18 ± 0.02 .

Introduction

The excited state manifolds of halocuprate(I) and cyanocuprate complexes are fairly well characterized [1–6]. The hydrated electron formation initiated by light absorption in the UV range occurs with a higher efficiency when two, rather than three, ligands are coordinated to the central atom of d^{10} electron configuration, as has been demonstrated in the case of both the halo and cyano complexes [7–16]. However, it is apparent that the luminescence occurs only in the aqueous solution of di- but not in that of the tricyanocuprate; whereas only the trihalocuprate appears to emit [2, 6, 14]. Regarding this contrasting behaviour it is expected that investigations of mixed ligand complexes might contribute to the elucidation of the physics and chemistry of the excited copper(I) compounds. Here we report some results of our investigations directed to identify and characterize the chlorodicyanocuprate(I) complex.

Experimental

All solutions were prepared to desired concentration from stock solutions of reagent grade NaCl,

NaClO_4 and NaNO_3 . The crystalline potassium salt of the dicyanocuprate(I) was prepared by the following method. Excess of the freshly prepared CuCN was added to the aqueous solution of KCN. The undissolved CuCN was filtered off. The bright white crystals were obtained by careful evaporation of water under decreased pressure of argon; washed with alcohol and ether then dried *in vacuo* at room temperature for 24 h; checked by C, N, Cu analysis and spectroscopic methods (UV–Vis, IR).

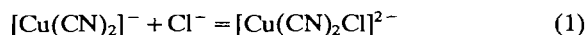
The solutions to be irradiated were deaerated with a stream of argon in a quartz cuvette with a volume of 4 cm³ and an optical pathlength of 1 cm. When N_2O was used as electron scavenger the sample was saturated with N_2O before irradiation.

Absorption measurements were performed with a Beckman ACTA MVI or a Hewlett Packard 8451A diode array spectrophotometer, both were fed to HP-86 microcomputer. Luminescence spectra were recorded on a Shimadzu RF-540 spectrofluorophotometer connected to a HP-86 microcomputer. Time resolved experiments were performed with a laser kinetic spectrometer given elsewhere [14]. Quantum yields for continuous photolysis were determined in a 1000 W irradiation system described previously [9]. The light intensity was measured with the ferrioxalate actinometer [17].

Results and discussion

Absorption spectra

The effect of varying the chloride ion concentration on the spectra was obtained by measuring a series of difference spectra between pairs of samples, both containing identical chloride ion concentrations but only one containing the dicyanocuprate(I) complex at a fixed concentration of 5×10^{-4} M. The concentration of the cyanocuprate(I) was at least two orders of magnitude lower than that of chloride, therefore the difference spectra should represent only the absorption of the copper complexes. The investigations were conducted at constant salt concentration (5 M) adjusted by addition of a suitable amount of sodium perchlorate. The spectra obtained between 200 and 300 nm clearly indicate the appearance of a new coordination species of copper(I) (Fig. 1), which possesses absorption bands in the UV rather different from those of either the pure dicyano- or any possible chlorocuprate(I) complex [4-6, 14, 15]. The coordination of the third cyano ligand to the copper(I) central atom leads to a larger difference between the highest and lowest spin- and symmetry-allowed $d \rightarrow \pi^*$ CTTL bands due to the increased splitting in d orbitals at higher ligand field strength. However, the observed spectra show an opposite tendency; hence, it is reasonable to assume the coordination of one chloride ion of low ligand field strength.



Using the measured absorbances, D , we calculated the value of the equilibrium constant, K , and the spectra of the equilibrated mixed ligand and dicyano complexes by finding the best fit to the following expression

$$D/cl = \epsilon_2 + (\epsilon_2 - \epsilon_3)/(1 + K[\text{Cl}^-]) \quad (2)$$

where c is the concentration of copper(I) in M, l is the optical path length in cm, ϵ_2 and ϵ_3 the molar absorbances of the dicyano and mixed ligand complexes, respectively, in $\text{M}^{-1} \text{cm}^{-1}$. The resulting optimum value of K at 5 M concentration of 1:1 electrolyte, 0.70 ± 0.12 , is essentially the same as the stepwise formation constant of trichlorocuprate(I) [2], suggesting rather similar changes in the coordination sphere of the copper(I) central atom in both reactions. Figure 2 shows the resulting calculated spectrum of $\text{Cu}(\text{CN})_2\text{Cl}^{2-}$, along with the resulting dicyano complex, which is virtually identical to the reported one [4-6, 18].

It should be noted that our interpretation based on spectral changes is in contrast to results of Cooper and Plane [19] who used Raman spectroscopy to conclude that no mixed ligand complexes are formed in solutions of cyanocuprate(I) complexes containing halide ions. However, our results cannot be explained in terms of cyanide displacement by halide ion, such as in the reactions

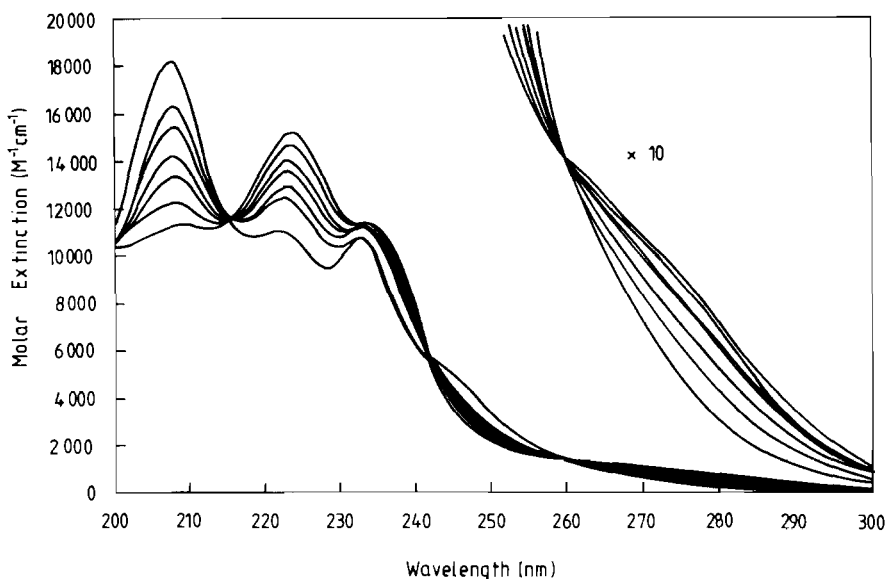
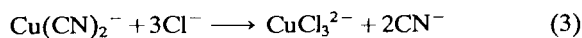


Fig. 1. UV absorption spectra of copper(I) complexes in aqueous solution of 5 M salt concentration; 5×10^{-4} M $\text{Cu}(\text{CN})_2^-$ and 0.2, 0.6, 1.0, 1.5, 2.0, 3.0, 5.0 M Cl^- . (The molar absorbances decrease between 200 and 216 as well as between 242 and 260 while decrease in ranges 216-242 and 260-300 nm with chloride concentration.)

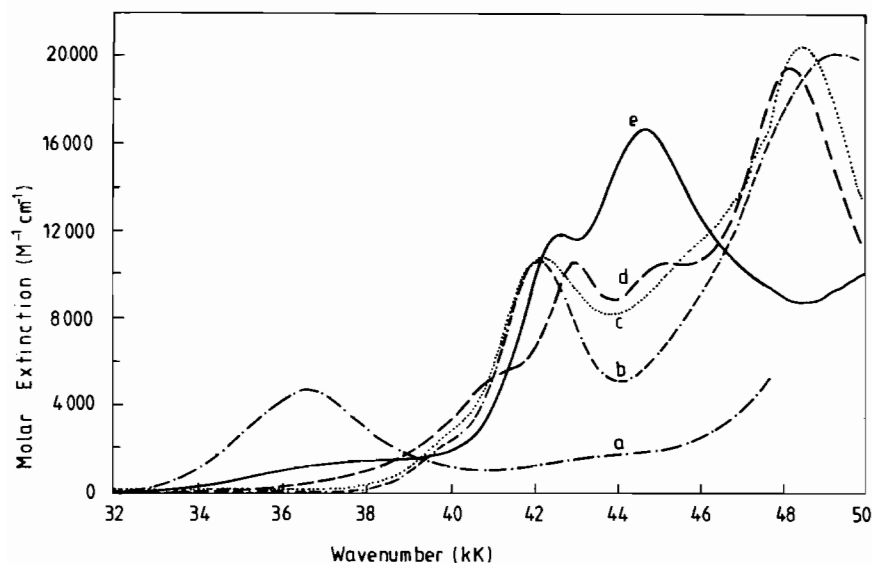
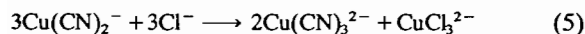


Fig. 2. UV absorption spectra of CuCl_3^{2-} (a), $\text{Cu}(\text{CN})_3^{2-}$ (b), $\text{Cu}(\text{CN})_4^{3-}$ (c), and the resolved spectra of $\text{Cu}(\text{CN})_2^-$ (d), and $\text{Cu}(\text{CN})_2\text{Cl}^{2-}$ (e) in 5 M ionic strength aqueous solutions.

or



since the equilibrium constants for these reactions would be too small (2×10^{-18} , 1.3×10^{-11} or 8.2×10^{-8} for reactions 3, 4 or 5, respectively, as calculated from published stability constants for the cyanocuprate(I) [20] and trichlorocuprate(I) [21] complexes). Moreover, it is clear that the spectra of tri- and tetracyanocuprate(I) complexes [6, 22], which have also been added to Fig. 2 for comparison (curves b and c), could not add to that of trichlorocuprate(I) in any combination to yield the spectrum of the postulated mixed ligand complex.

Luminescence investigations

Our luminescence results indicate that the weak emission of the excited dicyanocuprate(I) at 390 nm [6] disappears while a new luminescence band of lower intensity develops at 475 nm, with increasing chloride concentration as the new complex is formed (Fig. 3). It has been previously observed that such a quenching also occurs during the coordination of the third cyano ligand to $\text{Cu}(\text{CN})_2^-$ in aqueous solutions of low ionic strength [6]. Also, the bonding of the third chloride ion to the non-luminescent dichlorocuprate(I) results in the emission of the trichloro complex at 480 nm under UV excitation, especially at high ionic strength [2]. Both of these effects are observed during the formation of the mixed ligand complex.

The luminescence lifetime was determined by exciting the samples of various copper(I) concentration at 5 M NaCl with the pulsed laser flash at 266 nm and following the emission at 475 nm, yielding good first-order decay curves. The average of luminescence lifetime in these solutions, $\tau = 97.5 \pm 5.0$ ns, is nearly the same as that obtained for CuCl_3^{2-} in the same conditions, $\tau = 94.0 \pm 4.0$ ns. It should be mentioned that 107 ns was measured for CuCl_3^{2-} in a solution of 3 M NaCl [2], which is in good agreement with our results. The luminescence quantum yield calculated from emission measurements using quinine-sulfate in 1 N H_2SO_4 as reference [23] is $6.9 \pm 1.5 \times 10^{-4}$.

Photochemistry of the complex

Excitation of an aqueous solution of dicyanocuprate(I) in 5 M NaCl by a 266-nm laser pulse results in an immediate absorption peaking around 680 nm. Saturation of the sample with N_2O or by addition of NO_3^- ions to the solutions decreases the absorption and increases the decay rate in red. These observations lead to the assignment of the red absorbing species as hydrate electron.

In order to obtain the quantum yield for solvated electron formation the continuous photolysis of deaerated sample containing 5×10^{-3} M copper(I) was performed. The other solutes were 0.2 or 5 M NaCl, and the electron scavengers N_2O saturated at atmospheric pressure or 10^{-2} M NaNO_3 and 0.1 M NH_3 to indicate the formation of copper(II). Under

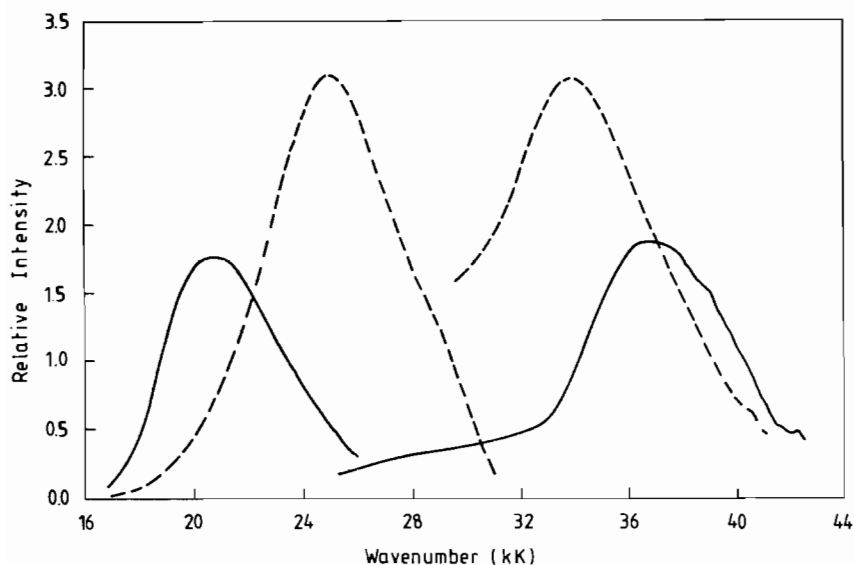
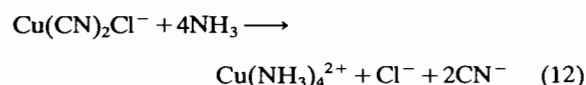
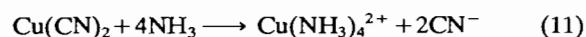
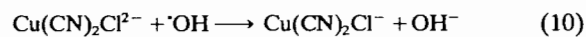
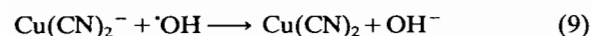
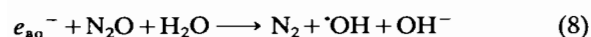
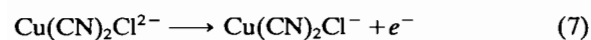
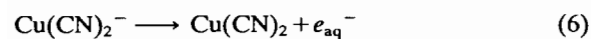


Fig. 3. Luminescence excitation and emission spectra of $\text{Cu}(\text{CN})_2^-$ (---) and $\text{Cu}(\text{CN})_2\text{Cl}^{2-}$ (—) at room temperature in solutions of 5 M ionic strength, 10^{-3} M $\text{Cu}(\text{CN})_2^-$, 0.1 M Cl^- (---) and 4.65 M Cl^- (—), monitored at 25 and 20.8 kK and excited at 33.9 and 36.4 kK, respectively.

UV irradiation the colorless solutions turn blue (Fig. 4), suggesting the formation of copper(II) ammine complex via the following reactions



However, in the presence of nitrate ions as electron scavengers the rate of tetraamminecopper(II) formation is half that obtained with N_2O (Fig. 5). This

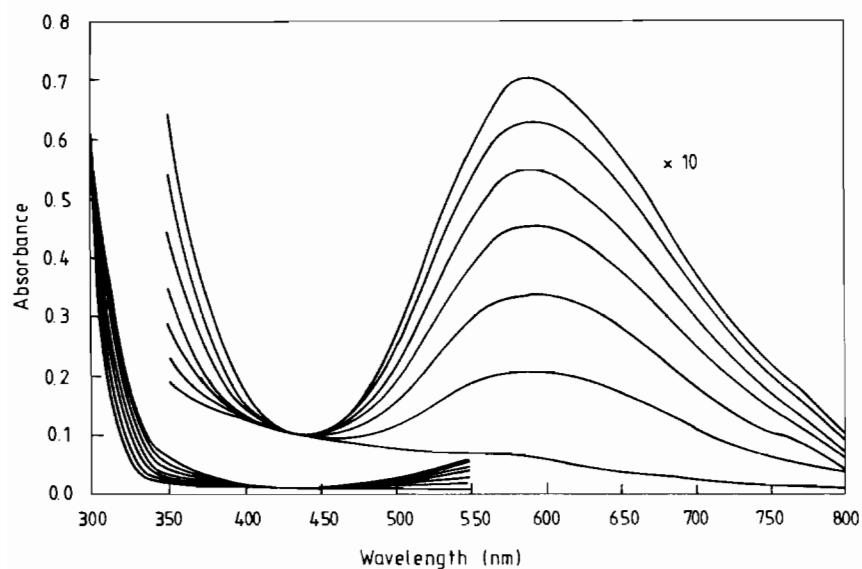


Fig. 4. Spectral changes in a solution of 5×10^{-3} M $\text{Cu}(\text{CN})_2^-$, 5 M NaCl and 0.1 M NH_3 under continuous UV irradiation in the presence of N_2O as electron scavenger.

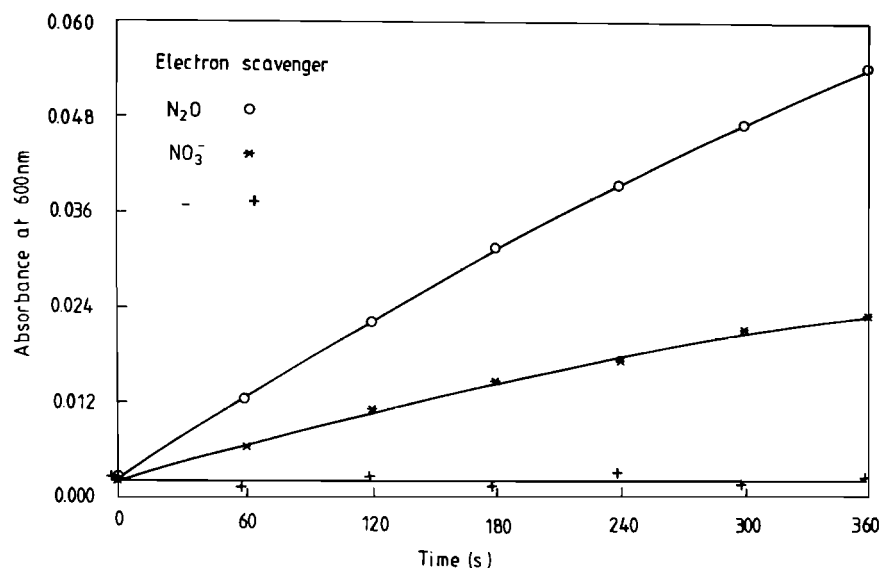
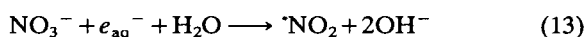


Fig. 5. Change in absorbance at 600 nm in aqueous solution of 5×10^{-3} M $\text{Cu}(\text{CN})_2^-$, 5 M NaCl and 0.1 M NH_3 under UV irradiation in the presence of electron scavengers.

indicates that the $\cdot\text{NO}_2$ radical formed in the electron scavenging reaction



does not oxidize the copper(I) complex cyanides, which is in accordance with our earlier proposal [6, 16]. The quantum yield for dicyanocuprate(I) and dicyanochlorocuprate(I) was calculated on the basis of overall quantum yields obtained from the initial slope of the kinetic curves (Fig. 5) by the procedure given elsewhere [6, 12, 16]; $\varphi_{\text{Cu}(\text{CN})_2} = 0.35 \pm 0.02$, $\varphi_{\text{Cu}(\text{CN})_2\text{Cl}} = 0.18 \pm 0.02$ at 254 nm. The former figure is nearly the same as obtained in diluted aqueous solutions of copper(I) cyanides [16], while the quantum yield of the mixed ligand complex is different from that of any chloro- or cyanocuprate(I) (Table 1). A comparison of quantum yields confirms the general tendency that the halo and pseudohalo cop-

per(I) complexes have lower quantum yield for solvated electron formation when their coordination number increases.

Further steady state and time resolved photochemical investigations are in progress to obtain more insight into the photochemistry of this new copper(I) complex.

Acknowledgements

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TABLE 1. Quantum yield of solvated electron formation for copper(I) complexes excited at 254 nm in aqueous solutions

Complex	Quantum yield	Conditions	Reference
$\text{Cu}(\text{CN})_2^-$	0.31 ± 0.01	diluted solution	16
	0.35 ± 0.02	5 M ionic strength	this work
$\text{Cu}(\text{CN})_3^{2-}$	0.03 ± 0.01	diluted solution	16
CuBr_2^-	0.67	1 M ionic strength	14
CuBr_3^{2-}	0.34	1 M ionic strength	14
CuCl_2^-	0.54	5 M ionic strength	2
CuCl_3^{2-}	0.12	5 M ionic strength	2
$\text{Cu}(\text{CN})_2\text{Cl}^-$	0.18 ± 0.02	5 M ionic strength	this work

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