

## FORMATION OF Cu(II)-DICYANDIAMIDE COMPLEXES IN NEUTRAL AND ACIDIC AQUEOUS SOLUTIONS

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**Abstract**—This work presents spectroscopic studies and electrochemical characterization of Cu(II)-dicyandiamide (DCDA) complex formation. The range of conditions leading to the precipitation of the complex is significantly larger than that presented in the literature. In all cases the stoichiometry of the compound is:  $[\text{Cu}(\text{DCDA})_2(\text{SO}_4)(\text{H}_2\text{O})_5]$ . The spectroscopic data suggest that DCDA is a monodentate ligand forming a bond with  $\text{Cu}^{2+}$  via the nitril nitrogen. Electroreduction of this complex is a two-step process occurring through a Cu(I)-DCDA intermediate.

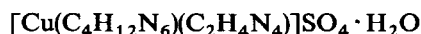
The formation of cupric complexes of dicyandiamide (DCDA) was first reported in 1906 and its stoichiometry was established as:  $[\text{CuSO}_4(\text{DCDA})_2(\text{H}_2\text{O})_4]$ .<sup>1</sup> In subsequent years a significant revival of interest in the chemistry of these complexes took place due to their catalytic role in the reaction of alcohol addition to the nitril group of DCDA.<sup>2,3</sup>

The complex studied previously was precipitated from the saturated aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and DCDA at 273 K and exhibited the formula:  $[\text{Cu}(\text{DCDA})_2\text{SO}_4]$  as determined by elemental analysis. Its structure and bonding were not studied and the only structural information presented was limited to the observation of a  $2222 \text{ cm}^{-1}$   $\nu(\text{C}^1 \equiv \text{N}^3)$  doublet in the IR spectra of the compound. Since this transition is characteristic of DCDA it was concluded that the nitril group of dicyandiamide does not participate in the complex formation and does not undergo hydrolysis under given conditions.

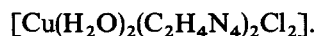
Cu(II), Ni(II) and Zn(II) complexes of DCDA were prepared in ethanol solutions and have a general formula:  $\text{MX}_2(\text{DCDA})_2$  or  $\text{MX}_2(\text{DCDA})_4$ , (where X = Cl, Br,  $\text{NO}_3$ , NCS).<sup>4</sup> In the case of X =  $\text{ClO}_4$  the formula  $[\text{Cu}(\text{DCDA})_4(\text{ClO}_4)_2]$  was proposed with  $\text{ClO}_4$  as an outershell anion. As determined by IR spectroscopy the  $3350\text{--}3000 \text{ cm}^{-1}$   $\nu(\text{N}^{5,6}\text{—H})$  bond remains unchanged upon complex formation, but  $\nu(\text{C}^1 \equiv \text{N}^3)$  and  $\nu(\text{C}^1\text{—N}^4)$  are shifted towards higher

and lower wavenumbers respectively. Based on the results presented above it was concluded that the complex is formed via the  $\text{N}^4$  nitrogen of the guanidine group, i.e. DCDA is a monodentate ligand. This conclusion can be additionally supported by the existence of the higher local dipole moment at this nitrogen atom,<sup>5</sup> i.e. the guanidine nitrogen should be the most susceptible to form bonds with the cupric ion.

In general in cupric complexes DCDA can act as a ligand in the presence of other ligands of various types. The following complexes have been reported:<sup>6,7</sup> 1-(2-aminoethyl)biguanide(dicyandiamide)Cu(II) sulphate monohydrate:



and dichlorodiaquobis(dicyandiamide)Cu(II):



Structural studies of the above complexes showed octahedral coordination of the cupric ion in both complexes. In the former both nitril nitrogen and the guanidine nitrogen are coordinated to the copper. In the latter case DCDA is a monodentate ligand forming a coordination bond with  $\text{Cu}^{2+}$  via the  $\text{N}^3$  nitrogen of the nitril group. Our studies of  $\text{Cu}^{2+}$  electroreduction in the presence of selected derivatives of guanidine led us to study Cu(II)-DCDA complex formation. To date no systematic spectroscopic studies and no electrochemical characterization of these compounds have been presented in the literature.

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Table 1. Elemental analysis of  $[\text{Cu}(\text{DCDA})_2(\text{SO}_4)(\text{H}_2\text{O})_5]$  complex

	Cu	H	C	N	S	SO <sub>4</sub>
Calc.	15.2	4.35	11.49	26.82	7.67	22.98
Exp.	15.2	4.28	11.51	25.41	7.97	24.5

## EXPERIMENTAL AND RESULTS

### Preparation of complex

Cupric complexes of DCDA were precipitated at room temperature by mixing saturated aqueous solutions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and DCDA. In some cases the complexes were precipitated from 0.4 M  $\text{H}_2\text{SO}_4$  or 0.4 M  $\text{K}_2\text{SO}_4$  aqueous solution. The light blue precipitates obtained were repeatedly washed with water and then dried at 323 K in the air. In all experiments reagents of analytical purity and redistilled water were used.

### Elemental analysis

C, H, N were determined by combustion analysis using a Perkin-Elmer Microanalyser Model 240. Cupric and additionally cuprous ions were analysed by spectrophotometry. Classical gravimetric analysis was used for sulphate determination. In no samples were cuprous ions detected. In Table 1 results of elemental analysis are presented. The following stoichiometry of the complex was assumed for the calculations:  $[\text{Cu}(\text{DCDA})_2(\text{SO}_4)(\text{H}_2\text{O})_5]$ .

### UV spectroscopy studies

UV spectroscopic studies were carried out for the neutral aqueous and acidic aqueous solutions of Cu-DCDA complexes. A UV-VIS (Karl-Zeiss Jena)

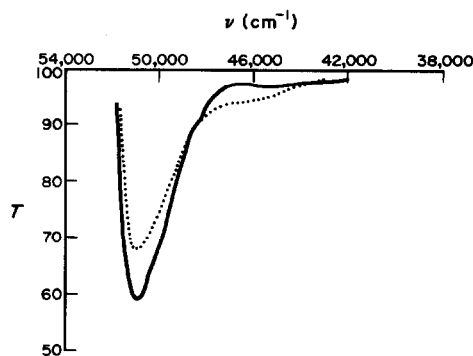


Fig. 1. UV spectrum of DCDA ( $2 \times 10^{-5}$  M in 0.4 M  $\text{H}_2\text{SO}_4$ —) and Cu-DCDA complex precipitated from 0.4 M  $\text{H}_2\text{SO}_4$  ( $1 \times 10^{-5}$  M in 0.4 M  $\text{H}_2\text{SO}_4$ ···).

spectrometer was used in all experiments. The solutions were loaded into rectangular quartz cuvette of the inner thickness of 1 cm. The results are summarised in Table 2 and Figs. 1-3.

Since guanyurea is the product of DCDA hydrolysis its spectrum was studied for comparison

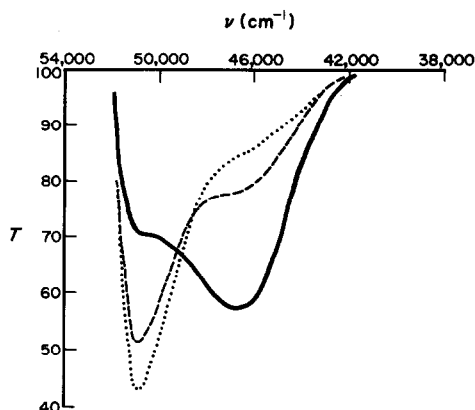


Fig. 2. UV spectrum of Cu-DCDA complex precipitated from 0.4 M  $\text{H}_2\text{SO}_4$  ( $1 \times 10^{-5}$  M in 0.4 M  $\text{H}_2\text{SO}_4$ —), the same solution after 7 days (---), after 12 days (···).

Table 2. UV optical parameters of pure and complexed DCDA

Substance	Medium	$\lambda_{\text{max}}$ (nm)	$\log \epsilon_{\text{max}}$	Reference
DCDA	Aqueous solution	216		8
		215		9
		215	4.13	
		192	3.90	10
		215.5	4.1	This work
Cu-DCDA complex (from aqueous solution)	0.4 M $\text{H}_2\text{SO}_4$	215*	4.1	This work
	Aqueous solution	216	4.4	This work
	0.4 M $\text{H}_2\text{SO}_4$	216	4.4	This work
Guanyurea	0.4 M $\text{H}_2\text{SO}_4$	197	4.4	This work

\* Maximum too broad to be determined precisely.

Table 3. IR spectroscopic parameters of DCDA and Cu-DCDA systems

Substance	H <sub>2</sub> N <sup>5,6</sup>	N <sup>3</sup> ≡C <sup>1</sup> —N <sup>4</sup> =	N <sup>5,6</sup> —C <sup>2</sup> =N <sup>4</sup>	Other	
DCDA (solid film <sup>11</sup> )	3350, 3320	2200, 2160	1590	3400, 2880	
	3170, 3140	1250	1500	2470, 2270	
	1660, 1640	528	930	2110, 1570	
	1080		720		
DCDA (KBr)	3380, 3330	2210, 2160	1570	3420, 2880	
	This work	3180, 3140	1255	1505	2740, 2105
		1660, 1640	555	930	670, 470
Cu-DCDA (from aqueous solution)	1090		720		
	3420, 3320	2250, 2210	1570, 1560	975, 675	
	3220, 3160	1300	1540	610, 470	
Cu-DCDA (from 0.4 M H <sub>2</sub> SO <sub>4</sub> )	1670, 1650	550	930	1110, 1040	
	3420, 3330	2260, 2210	1570, 1560	1720, 1710	
	3220, 3160	1300	1535	1350, 980	
Cu-DCDA (from 0.4 M K <sub>2</sub> SO <sub>4</sub> )	1675, 1650	550	930	675, 620, 450	
				1110, 1040	
	3420, 3320	2250, 2210	1570, 1560	975, 675	
	3320, 3160	1300	1530	610	
	1670, 1650	550	930	1110, 1050	

in order to exclude its presence in the reaction products. The appearance of a maximum at  $\lambda = 197$  nm was taken as a criterion for the hydrolysis reaction occurrence simultaneously with the complex formation reaction.

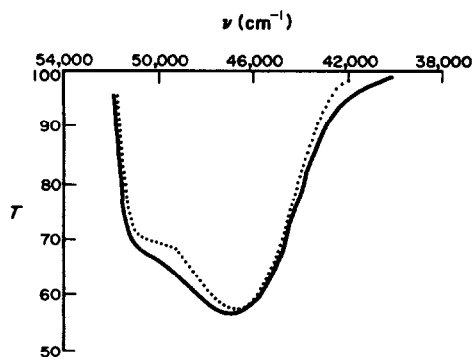


Fig. 3. UV spectrum of guanylurea ( $1 \times 10^{-5}$  M in 0.4 M H<sub>2</sub>SO<sub>4</sub>—) and DCDA solution ( $1 \times 10^{-5}$  M in 0.4 M H<sub>2</sub>SO<sub>4</sub>···) after 10 days.

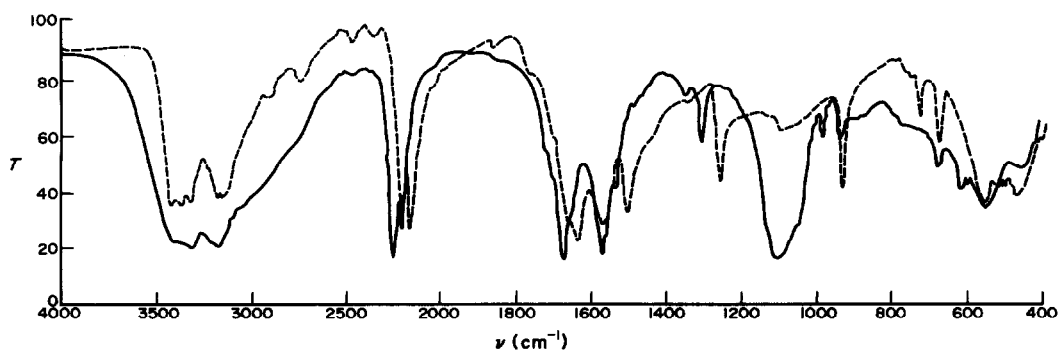


Fig. 4. IR spectrum of DCDA (---) and Cu-DCDA complex precipitated from 0.4 M H<sub>2</sub>SO<sub>4</sub> (—).

#### IR spectroscopy studies

A Perkin-Elmer IR Spectrometer was used to examine IR spectra of pure DCDA and Cu-DCDA complexes. KBr pressed pellets method was applied in all cases. Typical spectra, obtained from the acidic solution, are depicted in Fig. 4. All results of IR studies are summarised in Table 3.

#### Conductivity studies

Specific conductivities of 0.01 M aqueous solutions of Cu-DCDA complexes were measured at 291 K using O.K. 102/1 Conductivity Meter (Radelkis). As the reference, conductivities of identical CuSO<sub>4</sub> · 5H<sub>2</sub>O and pure DCDA solutions were measured. The results are listed in Table 4.

#### Polarographic studies

Square-wave Polarograph type OH104 (Radelkis) in two electrode configuration with mercury

Table 4. Results of specific conductivity measurements of DCDA,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and cupric complex of DCDA

Solution	Specific conductivity ( $10^3 \Omega^{-1} \text{cm}^{-1}$ )
Cu-DCDA (from aqueous solution)	1.33
Cu-DCDA (from 0.4 M $\text{H}_2\text{SO}_4$ )	1.47
Cu-DCDA (from 0.4 M $\text{K}_2\text{SO}_4$ )	1.22
DCDA	$4.0 \times 10^{-3}$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.16

dropping electrode and mercury pool as reference electrode was applied to study polarographic behaviour of Cu-DCDA complex. Constant concentration of cupric ions equal to  $10^{-5}$  M and varying concentrations of DCDA were employed in the polarographic investigations. 0.4 M  $\text{H}_2\text{SO}_4$  was used as supporting electrolyte. All measurements were performed at 293 K. The list of potentials, at which reduction peaks of the complexed copper ions appear, is presented in Table 5.

## DISCUSSION AND CONCLUSIONS

DCDA can form cupric complexes in neutral as well as in acidic aqueous solutions. In both cases identical blue powder of the same stoichiometry are obtained:  $[\text{Cu}(\text{DCDA})_2(\text{SO}_4)(\text{H}_2\text{O})_5]$  as shown by elemental analysis. It can be concluded therefore that the range of conditions leading to the precipitation of the complex is significantly larger than that presented previously.<sup>2</sup> This conclusion is highly consistent with the spectroscopic data showing that:

(1) Spectra of the complexes prepared under varying conditions are identical.

(2) Extinction coefficient ratio for "free" and "complexed" DCDA indicates the existence of two DCDA molecules per cupric cation in the complex.

(3) The main changes occurring in the IR spectrum

upon coordination can be characterized as follows: the band characteristic of  $\text{N}^4-\text{C}^1\equiv\text{N}^3$  skeleton observed at  $1255 \text{ cm}^{-1}$  in "free" DCDA is shifted to  $1300 \text{ cm}^{-1}$ . On the other hand the band characteristic of  $\text{N}^{5,6}-\text{C}^2=\text{N}^4$  skeleton is shifted from  $1570 \text{ cm}^{-1}$  to  $1530 \text{ cm}^{-1}$ . Additionally the change in the positions of the doublet associated with  $\text{C}^1\equiv\text{N}^3$  from 2210, 2160 to 2250, 2210  $\text{cm}^{-1}$  can be observed. Finally significant broadening of the bands ascribed to ammine groups is clearly seen. From the above observations it is concluded that DCDA is a monodentate ligand being coordinated to copper via the  $\text{N}^4$  nitrogen. This conclusion is consistent with the experimental facts presented before.<sup>5</sup>

The magnitude and direction of the shifts observed in the positions of selected IR bands are in good agreement with the values previously reported.<sup>4</sup> The position of the doublet characteristic of the nitril group<sup>2</sup> is very similar to the one measured in this work (Fig. 4).

However the conclusions drawn in both papers<sup>2,4</sup> do not necessarily need to be correct especially in view of the fact that the vibrations of  $\text{C}^1\equiv\text{N}^3$  group are shifted towards higher wavelength. If a metal acts as a Lewis acid and the coordination of DCDA via the lone pair of the  $\text{N}^3$  nitrogen will result in an increase in the frequency of the corresponding IR band.<sup>12</sup> It is therefore probable that DCDA forms a covalent bond with Cu(II) via the  $\text{N}^3$  nitrogen.

(4) In UV maxima of the absorption peaks in the "free" and "complexed" DCDA are identical.

(5) The shift of the absorption peak from 216 to 197 nm can be treated as a qualitative test of the hydrolysis leading to the formation of gunylurea.

(6) Existence of the  $1740 \text{ cm}^{-1}$  vibration mode (Fig. 4) in the IR spectrum additionally confirms the possibility of the hydrolysis of DCDA in acidic solutions. The above-mentioned absorption is characteristic of the carbonyl group of guanylurea.

(7) Polarographic studies of the Cu-DCDA complex led to the determination of its stoichiometry and the mechanism of the reaction occurring at the electrode. In a wide range of DCDA concentrations two one-electron peaks of the reduction could be

Table 5. Polarographic analysis data of Cu-DCDA complex

$\log c_{\text{DCDA}}$	-4.0	-3.301	-3.0	-2.301	-2.0	-1.301
$E_p\text{I (V)}$	-0.273	-0.225	-0.207	-0.110	-0.075	+0.030
$E_p\text{II (V)}$	-0.403	-0.409	-0.500	-0.567	-0.577	-0.609

$E_p(c_{\text{DCDA}} = 0) = -0.345 \text{ V}$ .

Potential sweep rate 2 mV/s.

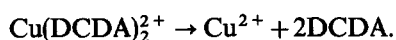
Amplitude of alternating voltage 20 mV.

Life-time of a drop 2.5 s.

observed. The potentials at which the above peaks occurred depended linearly on the ligand concentration. The first peak is associated with the  $\text{Cu(II)} + e \rightarrow \text{Cu(I)}$  reduction process. Its shape and measured half-width seem to suggest that the reduction process is irreversible. Its potential moves towards more positive values if the concentration of the ligand increases. The behaviour of the second peak, corresponding to the second stage of reduction,  $\text{Cu(I)} + e \rightarrow \text{Cu}$ , is different, its potential moves towards more negative values upon the increase of the ligand concentration. The process is quasi-reversible.

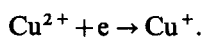
The above collected results seem to indicate that the reduction of Cu(II) in the presence of DCDA can be characterized by the following stages:

(a) Chemical stage—the dissociation of the complex:

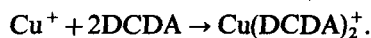


Since in 0.4 M  $\text{H}_2\text{SO}_4$  solution the Cu(II) and DCDA coexist in a form of a well-defined complex and in the polarographic process the simple Cu(II) ion is being reduced, the dissociation of the complex must precede the electrochemical process.

(b) Stage of charge-transfer E1:

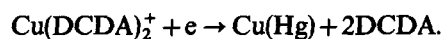


(c) Stage of the formation of  $\text{Cu}(\text{DCDA})_2^+$  complex:



Since in the second stage of the electroreduction process the cuprous ion, not in the simple but in the complex form, is being reduced, the formation of this complex must follow the stage E1. It is reasonable to believe that this formation occurs at the electrode surface and the adsorbed DCDA molecules participate in this process.

(d) Stage of charge-transfer E2:



The stoichiometry of the Cu(I)-DCDA complex and its stability constant  $\ln \beta_{\text{CuI}} = 6.9 \pm 0.3$  were derived from the relationships described in the literature.<sup>13</sup> In the calculations the experimental values of the potential shifts were assumed to be equivalent to the values of the reversible potentials of the half-wave in accordance with the arguments presented elsewhere.<sup>14</sup>

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