Formation of Glycine in the Hydrolysis of Coordinated Cyanogen

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It has been reported in the literature that under proper conditions the simultaneous coordination of cyanide and cyanogen is possible [1, 2]. Since in the early stage of chemical evolution both cyanide ion and cyanogen were among the common materials [3], it seems fairly likely that in this age cyanogen-containing cyanocomplexes could occur in the prebiotic soup and the behaviour of these complexes should be considered from the point of view of prebiotic syntheses.

We prepared a new cyanogen-containing complex and found that glycine is formed in its hydrolysis.

Results and Discussion

Preparation of the Complex $CuC_3N_3H_3O$

Originally we intended to prepare the dicyano-cyanogen-copper(I) complex described by S. K. Tobia *et al.* [1], but their experiment could not be quantitatively reproduced and only traces of the complex described by these authors could be obtained. However, we prepared a new complex with good yield according to the following synthetic procedure.

To a 60 ml 10 M sodium cyanide solution, cooled by an ice bath, 133 ml 1.5 M copper sulphate solution was added dropwise, under vigorous stirring. The colour of the solution turned to purple, then became brown and a brown material precipitated abundantly. The final molar ratio of Cu:CN$^-$ in the solution was 1:3. The precipitate was filtered off and washed with cold distilled water and finally dried over P_2O_5. The yield varied between 8 and 10 g.

The copper content of the complex was determined spectrophotometrically, while C, N, H and O were determined by elemental analysis. The data in parentheses are calculated values assuming the following composition $CuC_3N_3H_3O$: Cu: 39.8% (39.7); C: 21.8% (22.4); N: 25.8% (26.1); O: 8.0% (9.9); H: 1.6% (1.9).

When the complex is heated hydrogen cyanide and water are found in the range of temperature from 100 to 400 °C, while between 400 and 700 °C hydrogen cyanide, cyanogen and water are released, as shown by mass spectrometric analysis of the thermal-treatment products. This finding suggests that C_2N_2 may be coordinated to the metal. IR data support this proposal, in that a peak of high intensity at 2125 cm^{-1} and a shoulder at 2160 cm^{-1} can be observed in the IR spectrum of the complex both in nujol and KBr. The fact that there is no absorbance between 2330 and 2215 cm^{-1} in nujol makes it very likely that the cyanogen, if present in the complex, is not acting as a monodentate 'end-on' ligand [2, 4, 6]. The peak at 2125 cm^{-1} can be unambiguously assigned, in fact, to coordinated cyanide ions and the shoulder at 2160 cm^{-1} is proposed to be due to an 'end-on' bidentate bridging coordinated cyanogen. The absorption at 2160 cm^{-1} cannot be attributed, in fact, to terminal CN$^-$ ligands in copper(I) complexes [7]. A figure like 2160 cm^{-1} could be, in principle, only due to bridging CN$^-$ ligands, which do not appear to occur in copper(I) coordination chemistry [7]. The broad band between 3000 and 3500 cm^{-1} and a relatively sharp one at 1650 cm^{-1} indicate water of hydration.

Although at present no unambiguous structure can be given for the complex, the proposal that it contains terminal CN$^-$ and 'end-on' bidentate C_2N_2 as ligands seems very reasonable. A detailed structural study is in progress, in this paper only the peculiar hydrolysis of the complex is described.

0.1 g of the complex was boiled in 25 ml 1.0 M hydrochloric acid for 6 hours and the reaction mixture was analysed for amino acids by the usual paper and thin-layer chromatographic procedures. Only glycine could be detected. The quantity of glycine was determined spectrophotometrically [8]. Its amount was 3 mg, that is, 0.13 mol glycine was formed from one mol of coordinated cyanogen. Glycine was isolated as $H_2NCH_2COOC_2H_5 \cdot HCl$. From 3 g complex 88 mg glycine ethylester hydrochloric acid was obtained.

As is known, hydrolysis of cyanogen takes place according to the following reactions:

$$NCCN + 4H_2O = (COOH)_2 + 2NH_3 \quad \Delta G \sim 40 \, kcal$$
$$NCCN + H_2O = HCN + HNCO \quad \Delta G \sim 15 \, kcal$$
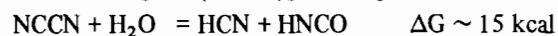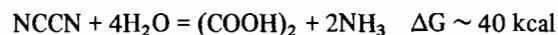
The formation of glycine can be accounted for by the following stoichiometry:

$$3NCCN + 6H_2O = H_2NCH_2COOH + 4HNCO + NH_3 \quad \Delta G \sim 80 \, kcal$$
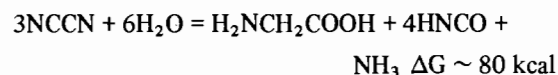
Apparently the coordination to the metal has a directing effect on the different thermodynamically possible hydrolytic paths.

It may be mentioned that the formation of glycine was observed in the reaction of cyanogen with hydrogen iodide in the past century [9]:

$$NCCN + 5HI + 2H_2O = NH_2CH_2COOH + NH_4I + 2I_2$$
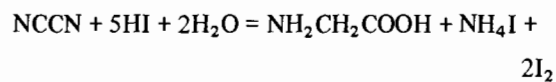
Although it is unlikely that the complex described had any role in chemical evolution, the formation of glycine in its hydrolysis indicated that the cyanogen complexes of transition metal ions are worth for study from a prebiotic point of view.

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