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# Characterization of a Copper(II) Complex Formed by Reaction of Acrylonitrile with N-Salicylideneglycinatocopper(II)

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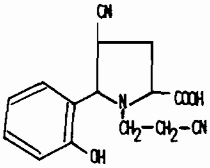
The reactivity of the methylene group in (α-amino acidato)metal complexes has been the subject of a number of investigations [1, 2]. Whilst the condensation of aldehydes is known in some detail [3 - 5], other reactions such as that with alkyl halides [6] or the Michael condensation of reagents containing activated double bonds [2, 7] has been reported only in a preliminary form.

We have investigated the reaction with acrylonitrile of Schiff base metal complexes of glycine with species like salicylaldehyde and pyruvic acid. In the case of N-salicylideneglycinatocopper(II),**, its treatment in anhydrous pyridine in the presence of triethylamine at room temperature with a stoichiometric amount of acrylonitrile produced two fractions: a small amount of a solid brown compound, separated by filtration from the reaction mixture, and a green solution which was evaporated to dryness. Successive slow crystallization from water of the latter residue gave dark green crystals together with some pale green powder.

The crystalline species, examined by X-ray diffraction,*** has been shown to contain a N-bonded cyanoethyl group (derived by N-alkylation of the glycine) and a proline-like ring derived by C-alkylation on the glycine methylene group and cyclization with the azomethine carbon atom. The compound obtained is therefore a copper(II) complex of N-(2-cyanoethyl)-4-cyano-5-*o*-hydroxyphenylproline:



The chelate complexes are linked, in the crystals, into infinite chains disposed along screw axes, the carboxylic group acting as a bridge with the oxygen atoms equally bound to two different copper atoms. Water solvating molecules are trapped in the cavities among the chains. A monomeric unit is shown in the Figure. The copper atom is five-coordinate by the tridentate macroligand, the carboxylic oxygen of a different unit and a water molecule. The coordination is a distorted square-pyramidal one, with the water molecule in the apical position. The three $O(H_2O)$–Cu–O(basal) angles are similar, with a mean value of 95°, while the $O(H_2O)$–Cu–N(1) angle is larger (105°). This enlargement, together with the marked deviation from linearity of the N(1)–Cu–O(3′) interaction (159°) with respect to the O(1)–Cu–O(2) one (171°), are indicative of steric repulsion between the apical water and the highly substituted nitrogen

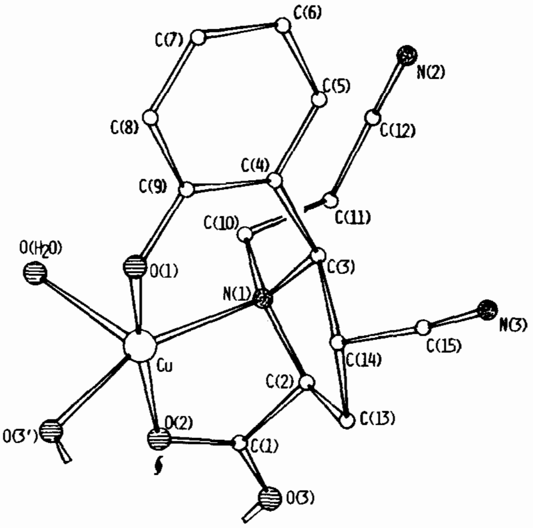


Figure. View of the asymmetric unit of the polymeric chelate complex. Bond lengths from the copper atom are: –N(1) 2.05(1), –O(1) 1.89(1), –O(2) 1.98(1), –O(3′) 2.02(1), $-O(H_2O)$ 2.22(1) Å.

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**Prepared according to ref. 8 and dried by azeotropic distillation with benzene.

****Crystal data.* $[Cu(C_{15}H_{13}N_3O_3)(H_2O)]\cdot nH_2O$, orthorhombic, space group $Pca2_1$(No. 29), $a$ = 20.21(2), $b$ = 13.11(1), $c$ = 7.19(1) Å, $U$ = 1905 Å$^3$, $Z$ = 4. The experimental density obtained by flotation, 1.50(3) g/cm$^3$, gives a formula weight for asymmetric unit of 430.1, which implies the presence of *ca.* 3.6 solvating water molecules. The intensity data were collected on a Pailred diffractometer, with graphite monochromatized Mo-$K_\alpha$ radiation ($\lambda$ = 0.7107 Å), within the limit $2\theta \leqslant 50°$. Absorption correction [$\mu$(Mo-$K_\alpha$) = 12.3 cm$^{-1}$] was performed. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares on the basis of 1238 independent reflections having $1 > 2\sigma(I)$. The copper atom was assigned an anisotropic thermal factor. Since some solvating water molecules are disordered their fractional occupations were also refined, the total number being in fair agreement with the observed density value. The refinements are in progress, the actual conventional $R$ factor being 7.3%.

atom. The *cis* angles between the basal atoms are in the range 83–95° and are similar to the corresponding angles in the parent N-salicylideneglycinatoaquocopper(II), reported in two differently hydrated structures [9, 10]. With respect to the parent species we have found, in the coordination sphere, the expected differences arising from the change in the hybridization state of N(1), in particular a lengthening of *ca.* 0.1 Å in the Cu–N(1) distance. Moreover it is noteworthy that, in both the above species, which exhibit a similar square-pyramidal coordination of the copper, the apical ligand is significantly more weakly bonded to the metal than in the present case.

The structure here reported is quite surprising because the use of the Schiff base metal complexes, in the kind of reactions described above, had been introduced to prevent N-alkylation [7, 11]. The nitrogen atom of the aminoacid Schiff base in N-salicylideneglycinatocopper(II) must be still basic enough to react with acrylonitrile, thus supporting an electronic arrangement of the ligand different from that of a normal metal-coordinated Schiff base. However, it is likely that the reaction is more complicated: N-alkylation and C-alkylation may occur separately; as a matter of fact glutamic acid could be detected by glc analysis [12] in the products of basic hydrolysis of the reaction mixture.

The nature of the brown material, which is insoluble in water, is presently under investigation; analytical data are not too different from those of the green fraction. Similar reaction products have been obtained in the case of the parent N-pyruvylideneglycinatocopper(II) complex.

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