

## LETTERS TO THE EDITOR

### PREPARATION AND PRELIMINARY X-RAY STUDIES OF ARGININE ASCORBATE, A CRYSTALLINE COMPLEX BETWEEN AN AMINO ACID AND A VITAMIN

ENZYME-COENZYME interactions, which are mostly noncovalent in character, are of considerable importance in biology. One approach to the study of the atomic details of such interactions is through the x-ray analysis of crystalline complexes between amino acids and short peptides on the one hand, and coenzymes and vitamins on the other. Here we report the preparation and preliminary x-ray analysis of such a complex between L-arginine and L-ascorbic acid (Vitamin C). Ascorbic acid is also known to function as a coenzyme in some enzymatic reactions. It may be mentioned that the work reported in this note constitutes the first attempt at the x-ray analysis of a crystalline complex between an amino acid and a vitamin or a coenzyme.

The crystals of L-arginine L-ascorbate were prepared by the slow evaporation of an aqueous solution of the components in molar proportions. In order to prevent the oxidation of ascorbic acid, the crystallization experiments were conducted inside a desiccator in nitrogen atmosphere. An alkaline solution of pyrogallol was placed in the desiccator to remove the residual oxygen. The composition of the crystals was confirmed by comparing the ultraviolet absorption spectrum of the crystals with those of the components.

The space group and the unit cell dimensions of the crystals were determined from oscillation and Weissenberg photographs, taken about crystallographic axes using  $\text{CuK}\alpha$  radiation. The density of the sample was measured by flotation in a mixture of benzene and carbon tetrachloride. These data are given below.

Space group  $P2_1$

$$a = 5.060 \pm 0.008, b = 9.977 \pm 0.009,$$

$$c = 15.330 \pm 0.013 \text{ \AA},$$

$$\beta = 97.5 \pm 0.2^\circ, D_m = 1.509 \pm 0.008,$$

$$D_c = 1.516 \text{ gr/cc}, Z = 2.$$

The complete structure determination of the complex is in progress.

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### DETERMINATION OF PHENANTHRIDINE IN NON-AQUEOUS MEDIA

PHENANTHRIDINE assumes importance as its salts are found to be remarkably active against trypanosome infections<sup>1</sup>. Very few methods are available for the determination of the base. In the present work an attempt has been made to determine phenanthridine in ethyl methyl ketone-acetic acid medium using chlorosulphonic acid by employing visual, photometric and potentiometric techniques.

Chlorosulphonic acid was purified by fractional distillation. Ethyl methyl ketone and acetic acid were purified by standard methods<sup>2,3</sup>. Phenanthridine was directly used after checking its melting point ( $108^\circ \text{C}$ ).

Approximately 1 M chlorosulphonic acid in acetic acid was diluted with ethyl methyl ketone to get the required concentrations. The solution was standardised by titration with anhydrous sodium acetate dissolved in the mixed solvent both potentiometrically and by visual titration.

In visual titrations 25 ml. of 0.02 M phenanthridine solution was titrated with 0.05 M chlorosulphonic acid using methyl orange indicator. The indicator produced light yellow colour in base solutions and bright pink in acid solutions.

In photometric titrations, 25 ml. of 0.0001 M phenanthridine solution was titrated against 0.01 M chlorosulphonic acid in presence of methyl red at 490  $m\mu$ .

In potentiometric titrations 25 ml. of 0.01 M base solution was titrated with 0.05 M chlorosulphonic acid. Glass electrode functioned as indicator electrode and the calomel electrode acted as reference electrode.

The experimental results obtained with the aid of the three different techniques are given in Table I.

TABLE I

	Phenanthridine		Error (%)
	Taken, mg	Found, mg	
Visual	17.92	17.96	+0.2
	8.96	8.92	-0.4
Photometric	0.89	0.89	0.0
	0.45	0.45	0.0
Potentiometric	8.96	8.96	0.0
	4.48	4.50	+0.4

The results show that chlorosulphonic acid could successfully be employed as a titrant for the determination of semi-micro quantities of phenanthridine.

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#### NICKEL (II) COMPLEXES OF SOME BIDENTATE AND TRIDENTATE SCHIFF BASES

THE chemistry of metal complexes of tridentate dibasic Schiff bases has received considerable attention in recent years<sup>1-3</sup>. Tridentate dibasic ligands force the M<sup>2+</sup> ions to form dimeric or polymeric metal complexes resulting in compounds with novel magnetic and spectral properties. In continuation of our work on tridentate dibasic Schiff bases<sup>4</sup> we

report in this communication the synthesis of several nickel (II) complexes of the Schiff bases (I) derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde and ethanolamine or propanolamine. The complexes have been characterised by elemental analysis, infrared and electronic spectra, conductance and magnetic susceptibility measurements.

The complexes were prepared by refluxing a mixture of nickel (II) acetate tetrahydrate (0.005 mole in 30 ml 95% ethanol) and the condensed Schiff base (0.005 mole in 20-40 ml ethanol 95%) on a steam bath for 2 hours. The separated compounds were filtered, washed with 95% ethanol and dried at 90° C for one hour. The complexes with N-(hydroxyalkyl)salicylideneimine were recrystallised from methanol or chloroform. The complexes with N-(hydroxyalkyl)-2-hydroxynaphthylideneimine are insoluble in common organic solvents. The complexes gave satisfactory elemental analysis.

The magnetic, infrared and electronic spectral data of the complexes are presented in Table I.

The complexes exhibit the  $\nu$  (OH) stretch in the region 3100-3300 cm<sup>-1</sup>. The observation of  $\nu$  (OH) stretch indicates the presence of coordinated water in [Ni(H<sub>2</sub>O)<sub>3</sub>L] complexes and of non-coordinated hydroxyl group of the coordinated ligands in [NiL'<sub>2</sub>]. The  $\nu$  (C=N) frequency of the complexes occurs in the range 1605-1630 cm<sup>-1</sup>. The shift of the  $\nu$  (C=N) frequency to lower wavenumber in comparison to the free ligands (1640 cm<sup>-1</sup>)<sup>5</sup> indicates the coordination of the Schiff bases through the nitrogen atom of the azomethine group. The magnetic moments (3.0 - 3.2 B.M.) of the hexa-coordinated complexes [Ni(H<sub>2</sub>O)<sub>3</sub>L] as determined by the Guoy method support the presence of an octahedral structure<sup>6</sup>. The tetra-coordinated complexes [NiL'<sub>2</sub>] are diamagnetic and a square planer structure can be assigned to these complexes<sup>8</sup>. The [Ni(H<sub>2</sub>O)<sub>3</sub>L] complexes exhibit two ligand field bands in methanol solution at about 10000 and

TABLE I

Magnetic, infrared and electronic spectral data of nickel (II) schiff base complexes

Complex	$\mu_{eff}$ B.M.	$\nu_{(C=N)}$ Cm <sup>-1</sup>	Medium	Absorption spectral data <sup>a</sup> , cm <sup>-1</sup>
[Ni (H <sub>2</sub> O) <sub>3</sub> salicylaldehyde-ethanolamine]	3.19	1630	methanol	16150 (8.1), 10500 (10.3)
[Ni (H <sub>2</sub> O) <sub>3</sub> (salicylaldehyde-propanolamine)]	3.29	1610	methanol	15050 (10.7), 9750 (7.6)
[Ni (hydroxynaphthaldehyde-ethanolamine) <sub>2</sub> ]	diamagnetic	1605	reflectance	17400, 16200
[Ni (hydroxynaphthaldehyde-propanolamine) <sub>2</sub> ]	diamagnetic	1605	reflectance	17400, 16300

<sup>a</sup> Figures in the parenthesis indicate  $\epsilon$ .