The Crystal Structure of Nitrato-bis(2,2′-bipyridine)copper(II) Nitrate Monohydrate $[Cu(NO_3)(bipy)_2]NO_3 \cdot H_2O$

Hisayoshi NAKAI, Shun'ichiro OOI and Hisao KUROYA

Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka

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It is well known that the reaction of Cu(II) with bipyridine gives three different products — the 1 : 1-, 1 : 2-, and 1 : 3-complexes — depending on the molar ratio of metal to ligand. Of these three, the structure of the 1 : 2-complex can be guessed to be *trans*-planar, as is shown in Fig. 1.

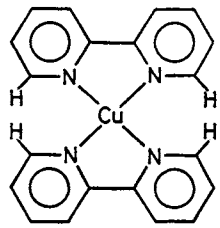

Fig. 1

However, the molecular model indicates that there must be a remarkable steric interference between the hydrogen atoms linked to the 3- and 3′-carbon atoms of the two bipyridine molecules. On the basis of his spectroscopic study, Jørgensen suggested that the complex has the *cis* configuration.[1] In order to elucidate the structure of the complex in detail, a single-crystal X-ray analysis has been carried out on $Cu(bipy)_2(NO_3)_2 \cdot H_2O$.

The blue crystals were prepared by Jaeger's method.[2] The unit cell has these dimensions:

$a=7.53$ $b=10.05$ $c=15.65$ Å
$\alpha=111.8°$ $\beta=91.0°$ $\gamma=90.5°$

The space group is $P\bar{1}$, with $Z=2$. The intensity data of $0kl$—$4kl$, $h0l$, $hk0$ were recorded on Weissenberg photographs ($CuK\alpha$ radiation) and were measured visually, the usual corrections being applied. The structure was solved by Patterson and Fourier techniques and refined by the block-diagonal least-squares method with isopropic temperature factors. The *R*-factor was 0.13 for 3087 independent reflections.

The crystal is essentially ionic and is composed of $[Cu(NO_3)(bipy)_2]^+$, NO_3^-, and H_2O. A schematic drawing of the complex ion is shown in Fig. 2. Four nitrogen atoms of the two bipyridine molecules and one of the oxygen atom of the coordinated nitrate ion form a distorted trigonal bipyramid around the copper atom. Cu, O_1, N_1, and N_3 are equatorially coplanar within the maximum deviation of 0.003 Å, making a dihedral angle of $\sim 10°$ with the O_1—$N_5\langle^{O_3}_{O_2}$ plane; N_5 and O_2 are distant by 0.20 Å, and O_3, by 0.39 Å, from the equatorial plane. The bipyridine molecules are necessarily in the *cis*-planar configuration, and their molecular dimensions are in good agreement with those found in the crystal of bipyridine.[3] The bond lengths and angles are listed in Table 1.

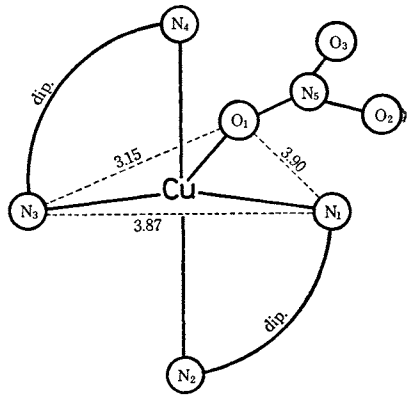

Fig. 2.

TABLE 1.

Bond length (Å)	Bond angle (degree)
$Cu-N_1=2.04$	$\angle N_4-Cu-N_1=99.3$
	$\angle N_2-Cu-O_1=85.9$
$Cu-N_2=2.01$	$\angle N_4-Cu-N_3=81.8$
	$\angle N_1-Cu-O_1=127.7$
$Cu-N_3=2.07$	$\angle N_4-Cu-O_1=85.4$
	$\angle N_3-Cu-O_1=91.9$
$Cu-N_4=1.99$	$\angle N_2-Cu-N_1=82.4$
	$\angle N_3-Cu-N_1=140.4$
$Cu-O_1=2.30$	$\angle N_2-Cu-N_3=103.3$

In the three-dimensional Fourier synthesis phased on the atomic coordinates of the complex ion, the electron density of the uncoordinated nitrate ion is rather more diffuse than that of the coordinated nitrate ion. The average temperature factor of the four atoms is 15 Å^2 in the former and 4.5 Å^2 in the latter. This fact suggests that the uncoordinated nitrate ion must be loosely bound in the crystal lattice.

1) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

2) F. M. Jaeger and J. A. Dijk, *Z. Anorg. Chem.*, **227**, 273 (1936).

3) L. L. Merritt, Jr., and E. D. Schroeder, *Acta Crystallogr.*, **9**, 801 (1956).