X-Ray Crystal and Molecular Structure of [Cu(nicotinamide)$_2$(H$_2$O)$_2$(BF$_4$)$_2$·2H$_2$O]

By Barbara L. Kindberg, Elizabeth H. Griffith, and Elmer L. Amma*
(*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208)

Summary The X-ray crystal and molecular structure of the complex [(nicotinamide)$_2$Cu(BF$_4$)$_2$.4H$_2$O] has shown that it contains isolated units of *trans* pseudo-octahedral Cu^{II} with two ring nitrogens from nicotinamide, two oxygens from water, and two fluorines from tetrafluoroborate making up the co-ordination polyhedron.

NICOTINAMIDE, the amide of the vitamin, is one of the two heterocyclic components of the essential co-enzymes NAD and NADP. Victims of pellagra, a disease caused by a deficiency of niacin, show unusually high serum and urinary copper levels.[1] It is thus of interest to determine the manner in which copper interacts with niacin and nicotinamide. The reaction of $Cu(BF_4)_2$ with nicotinamide and niacin was chosen in order to minimize anion interference. We report here the unusual product of one of these reactions. The complexes were prepared by mixing $Cu(BF_4)_2 \cdot xH_2O$ (1 g) with nicotinic acid (1 g) or nicotinamide (*ca.* 1 : 2 molar ratio) in aqueous solution in a plastic beaker (total volume *ca.* 75 ml). With nicotinic acid, a blue precipitate formed which decomposed on attempted recrystallization. Slow evaporation of the solution containing nicotinamide gave brilliant blue triclinic crystals. *Crystal data:* space group $F\bar{1}$, $a = 6{\cdot}743(0)$, $b = 16{\cdot}483(1)$, $c = 19{\cdot}340(2)$ Å, $\alpha = 98{\cdot}114(2)$, $\beta = 92{\cdot}973(2)$, $\gamma = 92{\cdot}539(2)°$, $D_m = 1{\cdot}72$ g cm^{-3}, $D_c = 1{\cdot}73$ g cm^{-3}, $Z = 4$.

A crystal, $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}2$ mm, mounted on a glass fibre gave 3900 reflections on a Picker automated diffractometer with Zr-filtered Mo-K_α radiation. 1912 of these were found to be non-zero at the 2·5 confidence level. The structure was solved by standard heavy-atom techniques and has been refined by full-matrix least-squares with anisotropic temperature factors to a current $R = 0{\cdot}089$.

The structure consists of isolated neutral molecules of $[Cu(nicotinamide)_2(H_2O)_2(BF_4)_2]$, with a *trans*-distorted octahedral environment about Cu^{II}. The nicotinamide rings are co-ordinated to the copper *via* the ring nitrogens. The fluorine atoms of BF_4^- occupy the axial positions of the distorted octahedron with the longest Cu–ligand bonds and the co-ordination polyhedron is completed by two water molecules. Two additional water molecules of hydration are unco-ordinated to the metal atom. Distances and angles within the ring compare well with other nicotinamide complexes [2–5] and nicotinamide[6] itself. The atomic co-ordinates and distances correspond to the $F\bar{1}$ cell for which parameters are given above.†

The structure shows several interesting features. The co-ordination of the tetrafluoroborate groups, while not unique, is still surprising in aqueous solution, especially with water molecules of solvation in the structure. This may be due to the extensive hydrogen bonding which apparently involves both types of water molecules, the amide groups, and two of the fluorines.

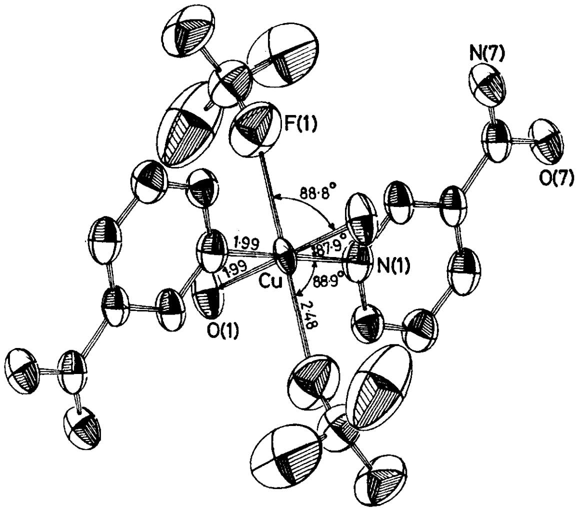

FIGURE. An ORTEP drawing of $[Cu(nicotinamide)_2(H_2O)_2(BF_4)_2 \cdot 2H_2O]$ showing the environment around the copper. The metal lies on a centre of symmetry and is co-ordinated to 2 water molecules, 2 nicotinamide rings, and 2 axial BF_4 groups. Two water molecules of crystallization are not shown. E.s.d.'s of distances shown are $\leqslant 0{\cdot}01$ Å and e.s.d.'s of angles shown are $\leqslant 0{\cdot}5°$.

While copper(II) complexes of isonicotinamide have been reported in solution,[7] and the crystal structures of Zn^{II},[2] Mn^{II},[3] and Cd^{II}[4] with *NN*-diethylnicotinamide and Zn^{II}[5] with nicotinic acid are known, this is the first structure reported of a metal complex of nicotinamide itself. The Mn^{II} and Cd^{II} complexes are bridged with co-ordination at both the amide oxygen and the ring nitrogen. This copper complex, like the zinc complex, involves co-ordination only at the ring nitrogen, and the amide group is involved only in an extensive network of hydrogen bonds.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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