Synthesis and Crystal Structure of Bis(*p*-aminobenzoate)2,2′-di-pyridylcopper(II)emiaquo

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Mixed-ligand complexes of copper(II) with molecules of biochemical interest such as amino acids have been studied in considerable detail [1–3] for their use as models in biological systems. *Para*-aminobenzoic acid, a constituent of folic acid, reacts with copper(II) salts to give bis(*p*-aminobenzoate)copper(II) [4], which cannot be obtained in crystals suitable for X-ray structure analysis.

We have investigated the effect of an additional ligand such as 2,2′-dipyridyl on bis(*p*-aminobenzoate)copper(II), and report here the synthesis and crystal structure of bis(*p*-aminobenzoate)2,2′-dipyridylcopper(II)emiaquo.

Experimental

The title compound $Cu(O_2CC_6H_4NH_2)_2bipy\cdot 0.5H_2O$ was prepared by mixing aqueous suspensions of bis(*p*-aminobenzoate)copper(II) (40 mg; 30 ml) and 2,2′-dipyridyl (16.4 mg; 10 ml) with a molar ratio of 1:1. The reaction mixture was stirred at 60 °C for several hours until a blue solution was obtained. The solution was reduced to *ca.* 20 ml. After two days, blue crystals suitable for X-ray analysis were separated; m.p. 260–262 °C.

Anal.: Found C, 57.4; H, 4.36; N, 11.36. Calcd. for $C_{24}H_{21}CuN_4O_{4.5}$: C, 57.5; H, 4.23; N, 11.18.

Crystal Data

$C_{24}H_{20}CuN_4O_4\cdot 0.5H_2O$, M = 501.0, monoclinic prisms, space group $C2/c$, a = 25.240(4), b = 11.924(2), c = 22.453(4) Å, β = 138.09(2)°, V = 4514(4) Å^3, D_c 1.474 g cm^{-3}, Z = 8, μ(Mo-Kα) = 10.08 cm^{-1}. 4057 intensity data were measured by a ω-scan technique on a Nonius CAD-4 automatic diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) in the θ range 3–25°. The structure, solved by conventional Patterson and Fourier methods, was refined by full-matrix least-squares, assigning anisotropic thermal parameters to all the non-hydrogen atoms and using 2583 independent absorption-corrected reflections having $I \geqslant 3\sigma(I)$. Final reliability indices values are R = 0.032 and R_w = 0.041. Relevant bond distances and angles with their e.s.d.s are reported in the caption of Fig. 1.

Results and Discussion

Crystals of the title compound consist of $Cu(O_2CC_6H_4NH_2)_2bipy$ and water molecules packed in space group $C2/c$. Since the water molecules lie on the crystallographic two-fold axis, the ratio between the copper complex and water is 2:1. As can be seen in the figure the coordination around the copper atom may be described as distorted square planar, with the two nitrogen atoms N(1) and N(2) of the dipyridyl ligand and the two carboxylic oxygens O(1) and O(3) as donor atoms. The extent of the distortion towards a tetrahedral coordination can be appreciated for instance from the dihedral angle of 19.3° between the N(1), Cu, O(1) and N(2), Cu, O(3) planes of the coordination sphere. The two remaining oxygen atoms O(2) and O(4) of the *p*-aminobenzoate ligands give two long, non-equivalent interactions with the copper atom (2.695(2) and 2.433(2) Å), thus completing a coordination polyhedron which can be described as a very distorted octahedron. The water molecule is involved in an intermolecular hydrogen bond with the O(2) atom ($O(2)\cdots H_{water}$ 2.14 Å, $O(2)\cdots H{-}O_{water}$ 163.6°). As usually found for other dipyridylcopper(II) complexes [5], the two Cu–N distances are slightly different, probably because of a small twisting (0.8°) of the two pyridinic rings with respect to each other around the C(1)–C(6) bond and of a tilting of the two planes (dihedral angle 1.8°).

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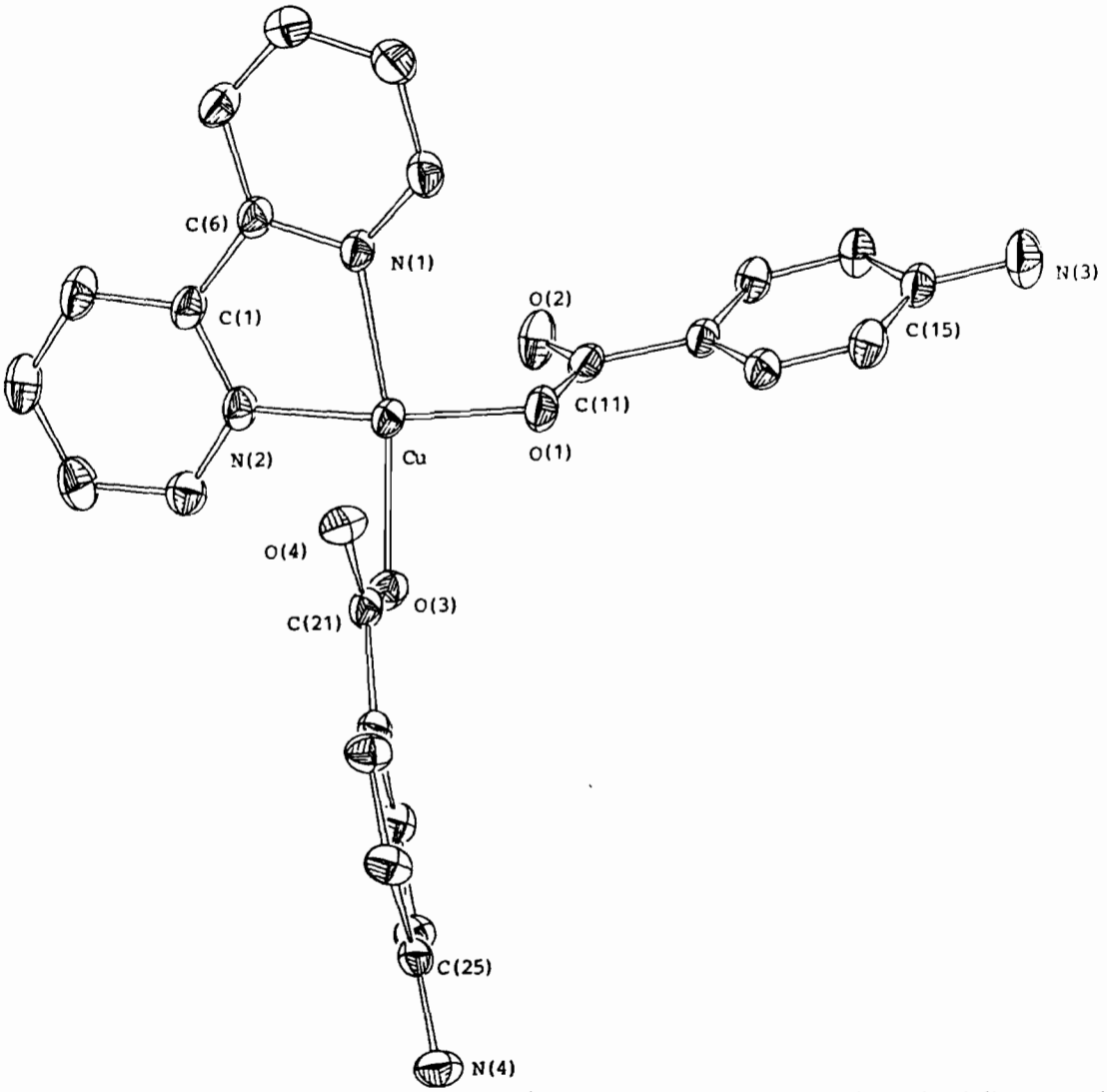

Fig. 1. ORTEP view of the bis(*p*-aminobenzoate)2,2′-dipyridylcopper(II) molecule. Relevant bond distances and angles are: Cu–N(1) 2.016(2), Cu–N(2) 1.982(2), Cu–O(1) 1.932(2), Cu–O(3) 1.993(2), C(11)–O(1) 1.280(4), C(11)–O(2) 1.231(4), C(21)–O(3) 1.278(3), C(21)–O(4) 1.248(3) Å, N(1)–Cu–N(2) 81.2(1), N(1)–Cu–O(1) 95.4(1), O(1)–Cu–O(3) 92.9(1), N(2)–Cu–O(3) 93.7(1), N(1)–Cu–O(3) 161.9(1), N(2)–Cu–O(1) 168.0(1)°.

References

1 L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chem., 21,* 1391 (1982).

2 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano and G. C. Pellacani, *Acta Cryst., B33,* 3886 (1977).

3 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chim. Acta, 46,* 107 (1980).

4 L. D'Ascenzo and A. D. Magri, *Termochim. Acta, 13,* 461 (1975).

5 R. J. Fereday, P. Hodgson, S. Tyagi and B. J. Hathaway, *J. Chem. Soc. Dalton,* 2070 (1981).