

- De Lima, G. M., Filgueiras, C. A. L., Giotto, M. T. S. & Mascarenhas, Y. P. (1995). *Transit. Met. Chem.* **20**, 380–383.
- Fait, J. (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Hayashi, T., Konishi, M., Kobori, Y., Kumada, M., Higuchi, T. & Hirotsu, K. (1984). *J. Am. Chem. Soc.* **106**, 158–163.
- Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1990b). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 347–348

trans-Diaquabis(4-hydroxybenzoato-*O*)bis-(nicotinamide-*N*)copper(II)

TUNCER HÖKELEK,^{a*} KIVANÇ BUDAK,^a KIVILCIM ŞENDİL^b
AND HACALI NECEFOĞLU^b

^aHacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and ^bKafkas University, Department of Chemistry, 63100 Kars, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr

(Received 16 May 1997; accepted 20 October 1997)

Abstract

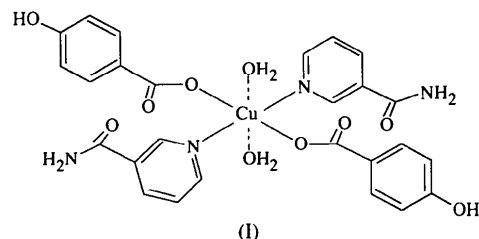
The title compound, $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$, is a crystallographically centrosymmetric complex in which pyridine N and carboxylate and water O atoms form a tetragonally Jahn–Teller-distorted octahedron about the Cu^{II} ion with bond distances of 1.956(2), 2.011(2) and 2.575(2) Å. The non-coordinated carboxylate O atoms form hydrogen bonds with the amide N and water O atoms [$\text{O} \cdots \text{O}$ 2.705(4) and $\text{O} \cdots \text{N}$ 2.888(3) Å].

Comment

Nicotinamide (NA) is one form of niacin and a deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). It is thus of interest to determine the manner in which copper interacts with niacin and nicotinamide. The structures of some complexes obtained from the reactions of Cu^{II} ions with nicotinamide have been determined; e.g. $[\text{Cu}(\text{sal})_2(\text{NA})_2]$ (sal is salicylate) (Hoang *et al.*, 1993) and $[\text{Cu}(\text{C}_7\text{H}_3\text{ClFO}_2)_2(\text{NA})_2]$ (Hoang *et al.*, 1995). In these complexes, NA is a monodentate ligand coordinated to Cu^{II} via its pyridine

N atom. In its rare earth complexes, NA is coordinated to the rare earth ion *via* only the O atoms of the substituents, not by the pyridine N atom (Poray-Koshits *et al.*, 1976). Coordination *via* the amide N atom may also occur. Hence, NA may function as a monodentate or bidentate ligand and may form molecular or polymeric structures affecting such properties of the compounds as their solubility.

For the complex $[\text{Cu}(p\text{-HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$, Shnulin *et al.* (1981) found a coordination number of five for the Cu^{II} ion. The three coordinated water molecules are located in the symmetry plane and the other two coordination sites are occupied by O atoms belonging to the carboxy groups of the two mirror-imaged acid ligands. The structure of the title molecule, (I), was determined in order to investigate the ligand properties of NA and the *p*-hydroxybenzoate ion, and compare the coordination geometries when the NA ligands are substituted for water in the Shnulin *et al.* (1981) complex.



The title compound is a monomeric complex with copper at a centre of symmetry. All ligands are monodentate. The pyridine N1 atoms of the two NA ligands and the O1 atoms of the two benzoate ions exhibit slightly distorted square-planar coordination to the Cu atom; the coordination is completed by two water O5 atoms at 2.575(2) Å to form a tetragonally Jahn–Teller-

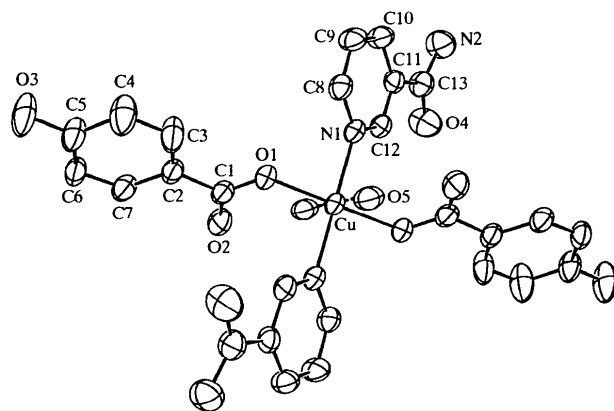


Fig. 1. An ORTEP (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

distorted octahedron (Fig. 1). There are hydrogen bonds between the carboxy O2 atoms, and the amide N2 and water O5 atoms [O2...N2 2.888 (3) and O2...O5 2.705 (4) Å]. In the carboxylate group, the C1—O1 bond is slightly longer than the C1—O2 bond, but not by as much as in the [Cu(*p*-HOC₆H₄COO)₂(H₂O)₃] complex [1.32 (1) and 1.22 (1) Å; Shnulin *et al.*, 1981]. It may also be observed that the Cu—N1 bond is shorter than in the dimeric complex [Cu₂(C₆H₅COO)₄(DNA)₂] [2.162 (6) Å; Hökelek *et al.*, 1995], but nearly the same as the corresponding distance in the monomeric complexes, *e.g.* [Cu(C₇H₄NO₄)₂(C₁₀H₁₄N₂O)₂(H₂O)₂] [2.019 (2) Å; Hökelek *et al.*, 1997].

Experimental

The title compound was prepared by reaction of [Cu(*p*-HO-C₆H₄COO)₂(H₂O)₈] (0.001 mol) and nicotinamide (0.001 mol) in an aqueous solution of ethanol. The mixture was set aside for crystallization at ambient temperature for a few days. Suitable deep-blue crystals were obtained by recrystallization from ethanol.

Crystal data

[Cu(C ₇ H ₅ O ₃) ₂ (C ₆ H ₆ N ₂ O) ₂ (H ₂ O) ₂]	Mo K α radiation
$M_r = 618.058$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	$\theta = 10-18^\circ$
$a = 11.4376$ (10) Å	$\mu = 0.853$ mm ⁻¹
$b = 9.8396$ (9) Å	$T = 298$ K
$c = 12.5356$ (11) Å	Plate
$\beta = 101.453$ (7) $^\circ$	0.30 \times 0.18 \times 0.08 mm
$V = 1382.7$ (2) Å ³	Deep blue
$Z = 2$	
$D_x = 1.4845$ Mg m ⁻³	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	2340 reflections with $F > 0$
$\omega/2\theta$ scans	$R_{int} = 0.027$
Absorption correction: empirical via ψ scans (<i>MolEN</i> ; Fair, 1990)	$\theta_{max} = 26.3^\circ$
$T_{min} = 0.843$, $T_{max} = 0.934$	$h = 0 \rightarrow 14$
3096 measured reflections	$k = 0 \rightarrow 12$
2777 independent reflections	$l = -15 \rightarrow 15$
	3 standard reflections every 250 reflections
	intensity decay: 1%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.056$	$\Delta\rho_{max} = 0.38$ e Å ⁻³
$wR = 0.044$	$\Delta\rho_{min} = -0.20$ e Å ⁻³
$S = 1.21$	Extinction correction: none

2340 reflections
239 parameters
H atoms refined isotropically
 $w = 1/\{\sigma^2(I) + (0.04F^2)^2\}^{1/2}(2F)^{-1}\}^2$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, $^\circ$)

Cu—O1	1.956 (2)	N1—C12	1.334 (3)
Cu—O5	2.575 (2)	N2—C13	1.318 (4)
Cu—N1	2.011 (2)	C1—C2	1.499 (3)
O1—C1	1.278 (3)	C2—C3	1.378 (3)
O2—C1	1.246 (3)	C2—C7	1.375 (4)
O3—C5	1.358 (3)	C3—C4	1.369 (4)
O4—C13	1.230 (3)	C4—C5	1.378 (5)
N1—C8	1.345 (3)		
O1—Cu—N1	92.0 (1)	C1—C2—C3	121.6 (2)
O5—Cu—N1	95.4 (1)	C1—C2—C7	120.7 (2)
O5—Cu—O1	88.9 (1)	N1—C8—C9	122.5 (2)
Cu—O1—C1	126.4 (1)	C10—C11—C12	117.7 (2)
Cu—N1—C8	125.1 (2)	C10—C11—C13	125.7 (2)
Cu—N1—C12	117.5 (2)	C12—C11—C13	116.6 (2)
C8—N1—C12	117.4 (2)	N1—C12—C11	123.9 (2)
O1—C1—O2	124.7 (2)	O4—C13—N2	122.8 (2)
O1—C1—C2	116.0 (2)	O4—C13—C11	119.3 (2)
O2—C1—C2	119.4 (2)	N2—C13—C11	117.9 (2)
O1—C1—C2—C3	-2.8 (4)	C10—C11—C13—O4	-170.8 (3)
O1—C1—C2—C7	175.5 (2)	C10—C11—C13—N2	9.4 (4)
O2—C1—C2—C3	178.2 (3)	C12—C11—C13—O4	9.4 (4)
O2—C1—C2—C7	-3.4 (4)	C12—C11—C13—N2	-170.3 (3)

The title structure was solved by the Patterson method. The H-atom positions were obtained from a difference map and refined isotropically.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1498). Services for accessing these data are described at the back of the journal.

References

- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Hoang, N. N., Valach, F. & Dunaj-Jurčo, M. (1995). *Acta Cryst.* **C51**, 1095–1097.
- Hoang, N. N., Valach, F. & Melník, M. (1993). *Z. Kristallogr.* **208**, 27–33.
- Hökelek, T., Budak, K. & Necefoğlu, H. (1997). *Acta Cryst.* **C53**, 1049–1051.
- Hökelek, T., Necefoğlu, H. & Balcı, M. (1995). *Acta Cryst.* **C51**, 2020–2023.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
- Poray-Koshits, M. A., Aslanov, L. A. & Korytniy, E. F. (1976). *Ser. Itogi Nauki Kristallokhim.* **11**, 5–94.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Shnulin, A. N., Nadzhafov, G. N. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1544–1555.