

Acta Cryst. (1995). **C51**, 1095–1097

Bis(2-chloro-6-fluorobenzoato)-bis(nicotinamide)copper(II)

NAM NHAT HOANG

Air Traffic Control Administration of the Slovak Republic, M. R. Stefanik Airport, 823 05 Bratislava, Slovakia

FEDOR VALACH*

Department of Chemical Physics, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia

MICHAL DUNAJ-JURČO

Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia

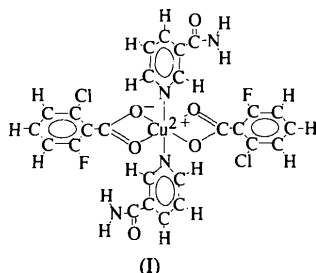
(Received 4 January 1994; accepted 29 November 1994)

Abstract

The crystal structure of the title compound contains centrosymmetric *trans*-[Cu(C₇H₃ClFO₂)₂(C₆H₆N₂O)₂] units held together by van der Waals forces. The coordination sphere around the Cu atom is a tetragonally deformed octahedron. Each Cu atom is coordinated by four O atoms [Cu—O 2.019 (3) and 3.141 (3) Å] and two N atoms [Cu—N 1.936 (6) Å]. The nicotinamides are monodentate, whereas the 2-chloro-6-fluorobenzoato ligands are asymmetrically bidentate with the carboxylate —COO[−] planes twisted nearly perpendicular to the plane of the substituted phenyl ring.

Comment

The title compound contains the 2-chloro-6-fluorobenzoato ligand which has not been structurally characterized previously. As part of a continuing study of copper(II)–nicotinamide complexes (Hoang, Valach & Melník, 1993) we report the structure of [Cu(2-Cl-6-FC₆H₃COO)₂(nia)₂] (nia is nicotinamide), (I).



Each Cu atom occupies a centre of symmetry and is surrounded by one N atom from each of the two nicotinamide ligands [Cu—N(1) 1.936 (6) Å] and one O atom from each of the two 2-chloro-6-fluorobenzoato ligands [Cu—O(1) 2.019 (3) Å], resulting in a *trans* square-planar configuration; the remaining two coordination positions around the Cu^{II} atom are occupied by a second pair of O atoms from the carboxylate groups of the two 2-chloro-6-fluorobenzoato ligands. According to Brown & Shannon (1973), the predicted Cu—O(2) bond length is 3.09 Å, which is very close to the observed value of 3.141 (3) Å. The coordination of Cu^{II} may, therefore, be described as pseudo-octahedral rather than square-planar. The weak Cu—O(2) bonding interaction may explain the orthogonal orientation of the plane through O(1), C(1) and O(2) to the least-squares plane through the substituted phenyl ring of the 2-chloro-6-fluorobenzoato ligand [dihedral angle 94.0 (2)°]. In most benzoates, the carboxylate and phenyl ring planes nearly coincide. The nicotinamide ring is planar ($\chi^2 = 5.3$), with the —CONH₂ group approximately in-plane, as in the structure of bis(salicylato)bis(nicotinamide)copper(II) (Hoang, Valach & Melník, 1993). In the crystal structure of pure nicotinamide (Wright & King, 1954), this group is significantly twisted from the plane of the nicotinamide ring. Mean C—C and C—N bond lengths [1.398 (1) and 1.350 (1) Å, respectively], and C—C—C and C—C—N angles [119.2 (2) and 120.7 (3)°, respectively] in the nicotinamide ring are very close to values found in similar complexes: re-

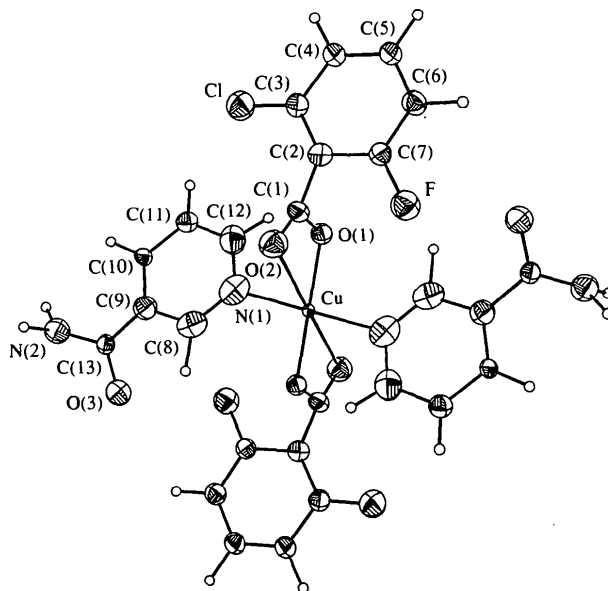


Fig. 1. The molecular structure of the title compound with displacement ellipsoids at the 50% probability level drawn using ORTEP (Johnson, 1965). H atoms are represented by spheres of arbitrary radii.

spectively, 1.396 (9) and 1.355 (5) Å, and 119.1 (5) and 121.1 (5)° in [Cu(H₂O)₂(BF₄)₂(nia)₂] (Kindberg, Griffith & Amma, 1977); 1.389 (7) and 1.334 (1) Å, and 118.5 (5) and 123.4 (5)° in [Cu₂(acetato)₄(nia)₂].2H₂O (Tsintsadze, Kiguradze, Shnulin & Mamedov, 1984); 1.382 (5) and 1.342 (3) Å, and 118.9 (2) and 122.5 (2)° in [Cu(H₂O)₂F₂(nia)] (Smolander, Macko, Valko & Melník, 1992); 1.39 (3) and 1.34 (2) Å, and 118.8 (3) and 123.1 (4)° in [Cu(CH₃CH₂COO)₂(nia)₂] (Smolander, Macko, Valko & Melník, 1992); 1.389 (7) and 1.392 (5) Å, and 120.0 (4) and 120.4 (5)° in [Cu(sal)₂(nia)₂] (sal is salicylate) (Hoang, Valach & Melník, 1993); and also values for [Cu(H₂O)₂F₂(nia)₂] (Emsley, Reza, Dawes & Hursthouse, 1986).

Experimental

The title compound was prepared according to the method of Melník, Sabová, Mrozinski & Szymaszek (1990). The density D_m was measured by flotation in CCl₄/CH₃Br.

Crystal data

[Cu(C₇H₃ClFO₂)₂-(C₆H₆N₂O)₂]

$M_r = 654.90$

Monoclinic

$P2_1/c$

$a = 7.435 (3) \text{ \AA}$

$b = 14.124 (3) \text{ \AA}$

$c = 13.693 (3) \text{ \AA}$

$\beta = 111.03 (3)^\circ$

$V = 1342.2 (7) \text{ \AA}^3$

$Z = 2$

$D_x = 1.62 \text{ Mg m}^{-3}$

$D_m = 1.63 \text{ Mg m}^{-3}$

Data collection

Syntex $P2_1$ four-circle diffractometer

Profile analysis of $\omega/2\theta$ scans

Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)

$T_{\min} = 0.306$, $T_{\max} = 0.654$

1834 measured reflections

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 15 reflections

$\theta = 4-10.5^\circ$

$\mu = 1.076 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.40 \times 0.30 \times 0.20 \text{ mm}$

Blue

1215 independent reflections

1185 observed reflections

$[F > 2\sigma(F)]$

$R_{\text{int}} = 0.02$

$\theta_{\text{max}} = 27.5^\circ$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 16$

2 standard reflections

frequency: 120 min

intensity decay: 0.4%

Refinement

Refinement on F

$R = 0.047$

$wR = 0.045$

$S = 1.13$

1185 reflections

187 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.03$

$\Delta\rho_{\text{max}} = 0.7 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.4 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Cu	0	0	0	1.06 (2)
O(1)	0.1536 (5)	0.0799 (2)	0.1242 (3)	2.6 (1)
O(2)	0.4368 (7)	0.0374 (3)	0.1311 (3)	4.3 (1)
O(3)	-0.0798 (7)	-0.3946 (3)	-0.0164 (3)	4.1 (1)
N(1)	0.0510 (9)	-0.1118 (4)	0.0876 (4)	5.5 (2)
N(2)	0.0743 (8)	-0.4493 (4)	0.1402 (4)	4.1 (2)
F	0.3942 (5)	0.2573 (3)	0.1095 (3)	4.4 (1)
Cl	0.4300 (3)	0.0426 (1)	0.3913 (1)	4.5 (1)
C(1)	0.3318 (9)	0.0760 (4)	0.1739 (4)	2.7 (2)
C(2)	0.4188 (8)	0.1500 (4)	0.2510 (4)	2.7 (2)
C(3)	0.4139 (9)	0.1338 (4)	0.3516 (4)	2.8 (2)
C(4)	0.3950 (8)	0.2140 (4)	0.4096 (4)	2.7 (2)
C(5)	0.3816 (9)	0.3027 (4)	0.3708 (4)	3.0 (2)
C(6)	0.3814 (9)	0.3174 (4)	0.2721 (4)	3.1 (2)
C(7)	0.3997 (8)	0.2429 (4)	0.2111 (4)	2.8 (2)
C(8)	0.062 (1)	-0.2011 (4)	0.0550 (5)	4.9 (3)
C(9)	0.0598 (9)	-0.2786 (4)	0.1185 (5)	3.6 (2)
C(10)	0.0454 (8)	-0.2629 (3)	0.2152 (4)	2.1 (2)
C(11)	0.0330 (9)	-0.1702 (4)	0.2482 (4)	3.1 (2)
C(12)	0.033 (1)	-0.0950 (5)	0.1807 (5)	4.9 (3)
C(13)	0.0190 (9)	-0.3771 (4)	0.0809 (4)	2.4 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cu—O(1)	2.019 (3)	C(2)—C(3)	1.410 (9)
Cu—O(2)	3.141 (3)	C(3)—C(4)	1.419 (8)
Cu—N(1)	1.936 (6)	C(4)—C(5)	1.350 (8)
O(1)—C(1)	1.255 (7)	C(5)—C(6)	1.367 (8)
O(2)—C(1)	1.256 (9)	C(6)—C(7)	1.380 (8)
O(3)—C(13)	1.294 (6)	C(7)—C(2)	1.409 (8)
N(1)—C(8)	1.350 (8)	C(8)—C(9)	1.401 (9)
N(1)—C(12)	1.349 (9)	C(9)—C(10)	1.384 (9)
N(2)—C(13)	1.276 (8)	C(9)—C(13)	1.477 (8)
Cl—C(3)	1.387 (6)	C(10)—C(11)	1.399 (7)
F—C(7)	1.392 (7)	C(11)—C(12)	1.408 (9)
C(1)—C(2)	1.461 (7)		
O(1)—Cu—N(1)	90.5 (2)	C(3)—C(4)—C(5)	121.9 (5)
Cu—O(1)—C(1)	126.9 (4)	C(4)—C(5)—C(6)	120.2 (5)
Cu—N(1)—C(12)	112.2 (5)	C(5)—C(6)—C(7)	121.2 (5)
Cu—N(1)—C(8)	125.4 (4)	C(6)—C(7)—C(2)	119.6 (5)
C(8)—N(1)—C(12)	120.9 (6)	C(6)—C(7)—F	121.3 (5)
C(2)—C(7)—F	119.1 (5)	N(1)—C(8)—C(9)	120.7 (6)
O(2)—C(1)—C(2)	117.3 (6)	C(8)—C(9)—C(10)	119.3 (5)
O(1)—C(1)—C(2)	117.9 (6)	C(8)—C(9)—C(13)	124.5 (6)
O(1)—C(1)—O(2)	118.5 (5)	C(10)—C(9)—C(13)	114.1 (5)
C(1)—C(2)—C(7)	115.4 (5)	C(9)—C(10)—C(11)	119.7 (5)
C(1)—C(2)—C(3)	115.5 (5)	C(10)—C(11)—C(12)	118.6 (5)
C(3)—C(2)—C(7)	119.7 (5)	C(11)—C(12)—N(1)	120.7 (6)
Cl—C(3)—C(2)	120.3 (5)	N(2)—C(13)—C(9)	123.5 (5)
C(2)—C(3)—C(4)	117.4 (5)	O(3)—C(13)—C(9)	120.6 (5)
Cl—C(3)—C(4)	122.3 (4)	O(3)—C(13)—N(2)	115.9 (5)

All H atoms were located from difference Fourier syntheses. They were assigned fixed isotropic displacement parameters and their positions were not refined.

Data collection: Syntex $P2_1$ built-in software. Cell refinement: Syntex $P2_1$ built-in software. Data reduction: XP21 (Pavelčík, 1987). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL76 (Sheldrick, 1976). Molecular graphics: ORTEP (Johnson, 1965). Software used to prepare material for publication: PARST (Nardelli, 1983).

This work was supported by the Slovak Ministry of Education and Science (Research Project No. 1/710/93). We thank Professor M. Melník and Mrs M. Sprušanská for preparation of the crystals.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* **A29**, 266–282.
 Emsley, J., Reza, N. M., Dawes, H. M. & Hursthouse, M. B. (1986). *J. Chem. Soc. Dalton Trans.* pp. 313–316.
 Hoang, N. N., Valach, F. & Melník, M. (1993). *Zeit. Krist.* **208**, 27–33.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Kindberg, B. L., Griffith, E. H. & Amma, E. L. (1977). *J. Chem. Soc. Chem. Commun.* **182**, 461–463.
 Melník, M., Sabová, Z., Mrozinski, J. & Szymaszek, A. (1990). *J. Mol. Struct.* **240**, 285–294.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Pavelčík, F. (1987). *XP21. Computer Program for Syntax P2₁ Data Reduction*. Faculty of Pharmacy, Comenius Univ., Bratislava, Slovakia.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Smolander, K., Macko, M., Valko, M. & Melník, M. (1992). *Acta Chem. Scand.* **46**, 29–30.
 Tsintsadze, G. V., Kiguradze, R. A., Shulin, A. N. & Mamedov, Kh. S. (1984). *Zh. Struct. Khim.* **25**, 82–86.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
 Wright, W. B. & King, G. S. D. (1954). *Acta Cryst.* **7**, 283–285.

Acta Cryst. (1995). **C51**, 1097–1099

Tetrakis(imidazole)copper(II) Dibromide, [Cu(Him)₄]Br₂

O. JERRY PARKER AND GARY L. BRENEAN

*Department of Chemistry and Biochemistry,
 Eastern Washington University, Cheney,
 WA 99004, USA*

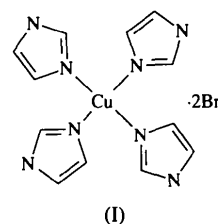
(Received 5 April 1994; accepted 7 October 1994)

Abstract

The structure of blue [Cu(C₃H₄N₂)₄]Br₂ consists of discrete [Cu(Him)₄]²⁺ ions (Him = imidazole), with the Cu atom on an inversion center [Cu—N 1.997 (4) and 2.008 (3) Å, N—Cu—N 89.9 (1) and 90.1 (1)°], and bromide ions [unique Cu···Br[−] 3.3767 (4) Å] in the fifth and sixth octahedral sites above and below the CuN₄ plane. The Br[−] ions also take part in a network of N—H···Br[−] hydrogen bonds [N···Br[−] 3.343 (4) and 3.383 (4) Å].

Comment

The [Cu(Him)₄]Br₂ complex has been prepared previously (Goodgame, Goodgame, Hayward & Rayner-Canham, 1968), and its vibrational bands, diffuse reflectance spectra and magnetic moment reported. The analogous iodide complex, [Cu(Him)₄]I₂, has also been prepared, and its molecular and crystal structure determined (Akhtar, Goodgame, Goodgame, Rayner-Canham & Skapski, 1968; Ballester, Parker & Breneman, 1993). The molecular determination of the iodide complex showed that the copper-to-iodide distances were long and unequal [3.406 (2) and 3.865 (2) Å (Ballester, Parker & Breneman, 1993)] in the pseudo tetragonal stereochemistry. The present work was undertaken in order to determine whether or not the analogous bromide complex, (I), had the same type of distorted tetragonal core.



An *ORTEP* (Johnson, 1965) plot of the complex is shown in Fig. 1 with the atomic numbering system. The structure consists of a discrete [Cu(Him)₄]²⁺ square-planar cation with two bromide anions, at best, weakly interacting with the copper(II) in the fifth and sixth octahedral positions. The Cu atom lies on an inversion center which requires the CuN₄ moiety of the cation to be precisely planar and also requires the Cu···Br distances to be equivalent. The Cu···Br distances of 3.3767 (4) Å are long for tetragonal copper(II) complexes. The compound CuBr₂ has short Cu—Br distances of 2.40 Å and long Cu—Br distances of 3.18 Å (Huheey, 1983). The complex [CuBr(NCS)(phen)₂] (phen = 1,10-phenanthroline) has a long Cu—Br distance of 2.820 (2) Å (Parker & Breneman, 1995) and the five-coordinate complex [CuBr(phen)₂]ClO₄ has a short copper-to-bromide distance of 2.496 (1) Å (Parker, Greiner, Breneman & Willett, 1994).

The Cu—N(Him) distances of 2.008 (3) and 1.997 (4) Å fall in the normal range for the equatorial bond lengths in tetragonal copper(II) complexes. These distances are comparable with those found in [Cu(Him)₄]I₂, [Cu(Him)₄SO₄], [Cu(Him)₄(ClO₄)₂], [Cu(Him)₄(H₂O)₂]F₂ and [Cu(Him)₄(NO₃)₂], with values of 1.996 (4)–2.026 (5), 2.000–2.021, 1.998–2.010, 1.984–2.033 and 2.008–2.018 Å, respectively (Ballester, Parker & Breneman, 1993; Fransson & Lundberg, 1972; Ivarsson, 1973; Vreugdenhil, Birker, ten Hoedt, Verschoor & Reedijk, 1984; McFadden, McPhail, Garner & Mabbs, 1976).