gram(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX95*.

This work was supported by NIH grant GM20488.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1040). Services for accessing these data are described at the back of the journal.

References

Cordes, A. W., Durham, B., Swepston, P. N., Pennington, W. T., Condren, S. M., Jensen, R. & Walsh, J. L. (1982). *J. Coord. Chem.* **11**, 251–260.

Downard, A. J., Honey, G. E., Phillips, L. F. & Steele, P. J. (1991). *Inorg. Chem.* **30**, 2259–2260.

Dunitz, J. D. (1979). In *X-ray Analysis and Structure of Organic Molecules*. Ithaca, NY: Cornell University Press.

Durham, B., Wilson, S. R., Hodgson, D. J. & Meyer, T. J. (1980). *J. Am. Chem. Soc.* **102**, 600–606.

Enraf–Nonius (1994). *CAD-4-PC Software*. Version 1.5. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Johnson, E. C., Sullivan, B. P., Salmon, D. J., Adeyemi, S. A. & Meyer, T. J. (1978). *Inorg. Chem.* pp. 2211–2215.

Kalyanasundaram, K. (1992). In *Photochemistry of Polypyridine and Porphyrin Complexes*. San Diego, California: Academic Press.

Acta Cryst. (1997). C**53**, 1049–1051

trans-Diaquabis(N,N-diethylnicotinamide-N^1)bis(4-nitrobenzoato-O)copper(II)

TUNCER HÖKELEK,[a]* KIVANÇ BUDAK[a] AND HACALI NECEFOĞLU[b]

[a]*Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and* [b]*Kafkas University, Department of Chemistry, 63100 Kars, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr*

(*Received 16 December 1996; accepted 1 April 1997*)

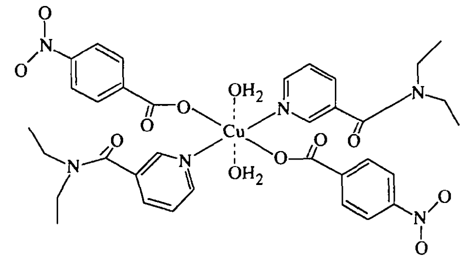
Abstract

The title molecule is a crystallographically centrosymmetric mononuclear complex containing two water molecules, two 4-nitrobenzoato and two diethylnicotinamide ligands, [Cu($C_7H_4NO_4$)$_2$($C_{10}H_{14}N_2O$)$_2$(H_2O)$_2$], all acting as monodentate ligands. The N and O atoms around the Cu atom form a square-planar arrangement, with the slightly tetragonally distorted octahedral coordination completed by two water O atoms at a distance of 2.485 (2) Å. The water molecules are hydrogen bonded to the carboxyl O atoms [O···O 2.705 (4) Å].

Comment

In the structure analysis of the copper complex of *p*-nitrobenzoic acid (Usubaliev, Amiraslanov, Mamedov & Movsumov, 1980), water molecules were placed in the channels formed by the dimeric [Cu_2(*p*-$O_2NC_6H_4COO$)$_4$(H_2O)$_2$] molecules, but two years later, Usubaliev (1982) pointed out that *p*-nitrobenzoic acid molecules were placed in the channels instead of water molecules. The dimeric structure was transformed to a monomeric structure when pyridine was used instead of water as solvent (Usubaliev *et al.*, 1981). Copper(II) benzoate forms both monomeric and dimeric complexes with the pyridine derivative *N*,*N*-diethylnicotinamide, DENA (Hökelek, Gündüz & Necefoğlu, 1996; Hökelek, Necefoğlu & Balcı, 1995).

The structure determination of the title copper complex with two water molecules, two DENA and two 4-nitrobenzoato ligands, (I), was undertaken to understand the effects of the $-NO_2$ and $-C(O)N(C_2H_5)_2$ substituents in the benzoic acid and pyridine molecules. The title monomeric complex, [Cu($C_6H_4COO.NO_2$)$_2$(DENA)$_2$.(H_2O)$_2$], has a centre of symmetry and the benzoate ligands are monodentate. The N atoms of the DENA and the O atoms of the benzoate groups form a square-planar coordination around the Cu atom (Table 1). The copper coordination geometry may be considered as slightly tetragonally distorted octahedral since Cu—O6 is 2.485 (2) Å and the angle between Cu—O6 and the normal of the Cu, N1, O1, N1′, O1′ plane is 3.1 (1)° (symmetry operator for primed atoms: $-x$, $-y$, $-z$).



(I)

There are hydrogen bonds between water molecules and the carboxyl O2 atoms [O···O 2.705 (4) Å]. Similar hydrogen bonds are observed in diaquabis[4-hydroxybenzoato)(*N*,*N*-diethylnicotinamide)]cobalt(II) [O···O 2.687 (5) Å; Hökelek & Necefoğlu, 1997], di(*p*-aminobenzoato)tetraaquacobalt(II) [O···O 2.592 (3) Å; Amiraslanov, Mamedov, Movsumov, Musaev & Nadzhafov, 1979] and di(*p*-nitrobenzoato)tetraaquacobalt(II)dihydrate (O···O 2.59 Å; Nadzhafov, Shnulin & Mamedov, 1981). The Cu atom lies 0.740 (2) Å out of the C1, C2, O1, O2 least-squares plane. The Cu—N1 bond length

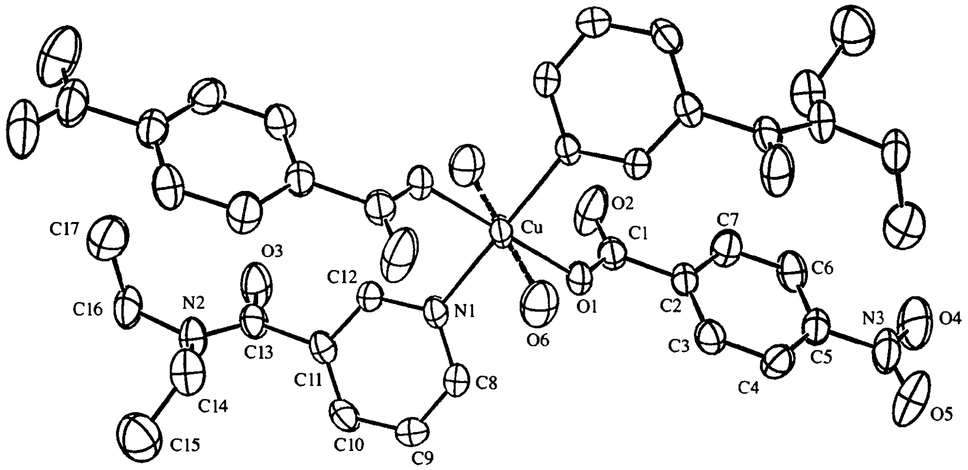


Fig. 1. The structure of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

between the Cu atom and the N heteroatom of the DENA molecule is shorter than in the dimeric complexes $[Cu_2(C_6H_5COO)_4(C_5H_5N)_2]$ [2.184 (7) Å; Usubaliev, Movsumov *et al.*, 1980] and $[Cu_2(C_6H_5COO)_4(DENA)_2]$ [2.162 (6) Å; Hökelek, Necefoğlu & Balcı, 1995], but almost equal to the corresponding distance in the monomeric complex $[Cu(C_7H_5O_2)_2(C_{10}H_{14}N_2O)_2]$ [2.004 (3) Å; Hökelek, Gündüz & Necefoğlu, 1996]. The Cu—O1 bond length [1.959 (2) Å] is slightly shorter than the average values reported for other monomeric and dimeric complexes; for example, 1.975 (5) Å in $[Cu(ClCH_2COO)_2(2\text{-pic})_2]$ (Davey & Stephens, 1971), 1.978 (5) Å in $[Cu_2(C_6H_5COO)_4(C_5H_5N)_2]$ (Usubaliev, Movsumov *et al.*, 1980), 1.974 (6) Å in $[Cu_2(C_6H_5COO)_4(DENA)_2]$ (Hökelek, Necefoğlu & Balcı, 1995) and 1.995 (2) Å in $[Cu(C_7H_5O_2)_2(C_{10}H_{14}N_2O)_2]$ (Hökelek, Gündüz & Necefoğlu, 1996).

The $-NO_2$ and $-C(O)N(C_2H_5)_2$ substituents cause significant variations in the bond angles of the benzoic acid and pyridine molecules with respect to the corresponding values in the benzoato group (Hökelek, Gündüz & Necefoğlu, 1996) and pure nicotinamide (Wright & King, 1954). The pyridine ring and the O3, C13, N2 plane form a dihedral angle of 66.6 (2)° with one another, which is smaller than in $[Cu(C_6H_5COO)_2(DENA)_2]$ [102.7 (1)°; Hökelek, Movsumov *et al.*, 1996] and $[Zn_2(PHB)_4(DENA)_2].2H_2O$ (where PHB is 4-hydroxybenzoato) [129.7 (2)°; Hökelek & Necefoğlu, 1996]. The dihedral angle between the planar carboxyl group (O1, C1, O2) and the planar phenyl ring (C2–C7) is 10.2 (7)°. The corresponding angles are 2.2 (6), 6.7 (9), 6.08, 7.12 and 5.10, and 1.3°, respectively, in $[Co(C_7H_5O_3)_2(C_{10}H_{14}N_2)_2(H_2O)_2]$ (Hökelek & Necefoğlu, 1997), $[Cu(C_6H_5COO)_2(DENA)_2]$ (Hökelek, Gündüz & Necefoğlu, 1996), $[Cu(PBN)_2(py)_2]$ (where PBN is *p*-nitrobenzoato) (Usubaliev *et al.*, 1981), $[Cu_2(C_6H_5COO)_4(py)_2]$ (Usubaliev, Movsumov *et al.*, 1980) and $[Cu(PHB)_2.8H_2O]$ (Shnulin, Nadzhafov & Mamedov, 1981).

Experimental

The title compound was prepared from the reaction of $[Cu_2(p\text{-}O_2NC_6H_4COO)_4(H_2O)_2].[0.25(p\text{-}O_2NC_6H_4COOH)]$ (0.001 mol) and DENA (0.0056 mol) in methanol (100 ml). The mixture was filtered and set aside for crystallization at ambient temperature for a few weeks. Suitable deep-blue crystals were obtained by recrystallization from ethanol.

Crystal data

$[Cu(C_7H_4NO_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$
$M_r = 788.269$
Triclinic
$P\bar{1}$
$a = 7.4083 (1)$ Å
$b = 8.5172 (1)$ Å
$c = 14.9425 (1)$ Å
$\alpha = 87.42 (1)°$
$\beta = 78.71 (1)°$
$\gamma = 77.57 (1)°$
$V = 902.89 (5)$ Å^3
$Z = 1$
$D_x = 1.4497$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9\text{–}18°$
$\mu = 0.676$ mm^{-1}
$T = 298$ K
Plate
0.33 × 0.28 × 0.16 mm
Deep blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.807$, $T_{max} = 0.897$

2747 reflections with $F > 0.5\sigma(F)$
$R_{int} = 0.027$
$\theta_{max} = 26.3°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$

3966 measured reflections
3667 independent reflections

3 standard reflections
every 250 reflections
intensity decay: 1%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.048$
$S = 1.17$
2747 reflections
249 parameters
H atoms riding

$w = 1/\{[\sigma^2(I) + (0.04F^2)^2]^{1/2}/(2F)\}^2$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.959 (2)	N1—C12	1.341 (4)
Cu—O6	2.485 (2)	N2—C13	1.336 (4)
Cu—N1	2.019 (2)	N2—C14	1.471 (4)
O1—C1	1.267 (3)	N2—C16	1.467 (4)
O2—C1	1.237 (4)	N3—C5	1.472 (4)
O3—C13	1.229 (3)	C1—C2	1.509 (4)
O4—N3	1.213 (4)	C11—C13	1.510 (4)
O5—N3	1.213 (4)	C14—C15	1.485 (6)
N1—C8	1.341 (4)	C16—C17	1.503 (6)
C8—N1—C12	118.2 (2)	O1—C1—C2	115.4 (2)
C13—N2—C14	124.2 (3)	O2—C1—C2	118.3 (3)
C13—N2—C16	118.2 (2)	N1—C8—C9	121.7 (3)
C14—N2—C16	116.2 (2)	C10—C11—C13	124.6 (2)
O4—N3—O5	123.7 (3)	C12—C11—C13	116.7 (3)
O4—N3—C5	117.7 (3)	O3—C13—N2	123.4 (3)
O5—N3—C5	118.6 (3)	O3—C13—C11	117.5 (3)
O1—C1—O2	126.3 (3)	N2—C13—C11	119.1 (2)

The structure was solved by the Patterson method. The positions of the water H atoms were obtained from a $\Delta\rho$ map and refined isotropically. The other H-atom positions were calculated geometrically with $U_{eq}(H) = 1.3U_{eq}$ of the parent non-H atom and a riding model was used in the refinement.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of a CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1457). Services for accessing these data are described at the back of the journal.

References

Amiraslanov, I. R., Mamedov, Kh. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979). *Zh. Strukt. Khim.* **20**, 1075–1080.

Davey, G. & Stephens, F. S. (1971). *J. Chem. Soc. A*, pp. 1917–1919.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Hökelek, T., Gündüz, H. & Necefoğlu, H. (1996). *Acta Cryst.* C**52**, 2470–2473.

Hökelek, T. & Necefoğlu, H. (1996). *Acta Cryst.* C**52**, 1128–1131.

Hökelek, T. & Necefoğlu, H. (1997). *Acta Cryst.* C**53**, 187–189.

Hökelek, T., Necefoğlu, H. & Balcı, M. (1995). *Acta Cryst.* C**51**, 2020–2023.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Nadzhafov, G. N., Shnulin, A. N. & Mamedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–128.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Shnulin, A. N., Nadzhafov, G. N. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1544–1555.

Usubaliev, B. T. (1982). Dissertation for the Degree of Candidate of Chemical Sciences, Institute of Inorganic and Physical Chemistry, Academy of Sciences AzSSR, Baku, Azerbaijan.

Usubaliev, B. T., Amiraslanov, I. R., Mamedov, Kh. S. & Movsumov, E. M. (1980). *Dokl. Akad. Nauk AzSSR*, **36**, 40–42.

Usubaliev, B. T., Amiraslanov, I. R., Nadzhafov, G. N., Movsumov, E. M., Musaev, F. N. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 440–444.

Usubaliev, B. T., Movsumov, E. M., Musaev, F. N., Nadzhafov, G. N., Ammiraslanov, I. R. & Mamedov, Kh. S. (1980). *Koord. Khim.* **6**, 1091–1096.

Wright, W. B. & King, G. S. D. (1954). *Acta Cryst.* **7**, 283–288.

Acta Cryst. (1997). C**53**, 1051-1054

Isostructural Complexes of Diiodo(phthalocyaninato)germanium(IV) and Diiodo(phthalocyaninato)tin(IV)

KRZYSZTOF EJSMONT AND RYSZARD KUBIAK

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, PO Box 937, Poland. E-mail: kubiak@highscreen.int.pan.wroc.pl

(*Received 16 January 1997; accepted 26 March 1997*)

Abstract

New diiodo(phthalocyaninato-κ^4)germanium(IV), $[GeI_2(C_{32}H_{16}N_8)]$ ($GePcI_2$, where Pc = $C_{32}H_{16}N_8$), and diiodo(phthalocyaninato-κ^4)tin(IV), $[SnI_2(C_{32}H_{16}N_8)]$ ($SnPcI_2$), complexes have been obtained. The phthalocyanine residues are centrosymmetric and are not staggered but slipped. In both cases, the phthalocyanine ring is not strictly planar. The *M*—I axis is tilted 1.9° in $GePcI_2$ and 3.0° in $SnPcI_2$ from the normal to the N_4-isoindole plane. In both compounds, the metal atoms (Ge and Sn) lie on inversion centers and are octahedrally coordinated by the four isoindole N and the two I atoms.

Comment

The crystals of $GePcI_2$, (1), and $SnPcI_2$, (2), are built from molecules of the title compounds (Fig. 1), with the intermolecular I···H contacts as shown in Fig. 2. The