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trans-Diaquabis(3-hydroxybenzoato-*O*)bis(nicotinamide-N^1)cobalt(II)

TUNCER HÖKELEK[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*

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Abstract

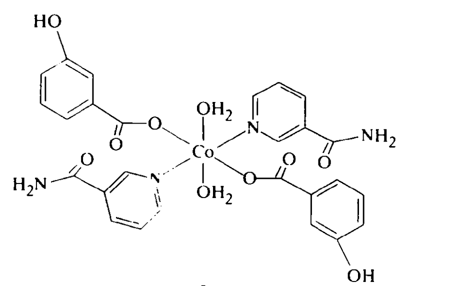
The title compound, $[Co(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$, is a monomeric and centrosymmetric cobalt complex. It contains two 3-hydroxybenzoate anions, two nicotinamide (NA) molecules and two water molecules as ligands. Each ligand is monodentate. The two nearest carboxylate O atoms and the two water O atoms form a slightly distorted square-planar arrangement around the Co atom [with distances of 2.099 (3) and 2.132 (3) Å, respectively], while the distorted octahedral coordination is completed by the pyridine N atoms of the NA ligands at a distance of 2.139 (4) Å. There is an intramolecular hydrogen bond between the nicotinamide N and O atoms [N···O 2.228 (6) Å], and the hydroxybenzoate and water O atoms form inter- [2.662 (5) Å] and intramolecular [2.586 (5) Å] hydrogen bonds, respectively, with the non-coordinated O atom of the carboxylate group.

Comment

Nicotinamide (NA) is a form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. The nicotinic acid derivative *N*,*N*-diethylnicotinamide (DENA) is an important respiratory stimulant. There are only a few examples of structure determinations of Co^{II} complexes with nicotinic and/or benzoic acid derivatives as ligands, *e.g.* $[Co(C_7H_5O_2)_2(NA)_2(H_2O)_2]$ [(II), where NA is nicotinamide, $C_6H_6N_2O$; Hökelek & Necefoğlu, 1999], $[Co(C_7H_4NO_4)_2(NA)_2(H_2O)_2]$ [(III); Hökelek & Necefoğlu, 1998], $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)]$ [(IV), where DENA is diethylnicotinamide, $C_{10}H_{14}N_2O$; Hökelek & Necefoğlu, 1997], $[M(C_7H_4NO_5)_2(H_2O)_4]$ [(V), where M = Zn^{II} and Co^{II}; Tahir *et al.*, 1997], $[Co(CH_3CO_2)_2(DENA)_2(H_2O)_2]$ [(VI); Mikelashvili, 1982] $[Co(p\text{-}O_2NC_6H_4COO)_2(H_2O)_4]$ [(VII); Nadzhafov *et al.*, 1981] and $[Co(p\text{-}H_2NC_6H_4COO)_2(H_2O)_4]$ [(VIII); Amiraslanov *et al.*, 1979].

The structure–function–coordination relationships of the arylcarboxylate ion in Co^{II} complexes of benzoic acid derivatives depend on the nature and position of the substituted groups in the phenyl ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Adiwidjaja *et al.*, 1978; Amiraslanov *et al.*, 1979; Nadzhafov *et al.*, 1981; Antsyshkina *et al.*, 1980). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). The crystal structure of complex (VI) is isostructural with the analogous Ni, Mn, Zn and Cd complexes (Sergienko *et al.*, 1980). In complexes (VII) and (VIII), the Co atoms are situated at centres of symmetry and are surrounded by six O atoms, forming slightly distorted octahedra. Four positions are occupied by water molecules and the other two by O atoms of the carboxyl groups of *p*-nitrobenzoate and *p*-aminobenzoate anions. In complexes (II) and (III), the Co atoms are also situated at centres of symmetry and are surrounded by four O atoms, forming slightly distorted square-planar arrangements, the distorted octahedral coordinations being completed by the pyridine N atoms of NA.

The structure determination of the title compound, (I), was undertaken to determine the ligand properties of NA and benzoate moieties and to compare the coordination geometries when the NA ligands are substituted by water, *i.e.* complexes (VII) and (VIII). The monomeric $[Co(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ molecules have the typical structure of NA complexes in which the metal atom has a *trans*-octahedral coordination. The complex has a centre of symmetry with the monodentate benzoate ions and NA ligand acting as monodentate ligands (Fig. 1). The four nearest symmetry-related carboxylate and water O atoms, with distances of 2.099 (3) and 2.132 (3) Å, respectively, form a slightly distorted square plane around the Co atom, while the slightly distorted octahedral arrangement is completed by the pyridine N atoms of NA ligands at distances of 2.139 (4) Å.



(I)

There are hydrogen bonds between the water O1 and carboxylate O3 atoms [O1···O3 2.586 (5) Å]. Similar hydrogen bonds are observed in (II) [2.580 (2) Å], (III) [2.634 (5) Å], (IV) [2.687 (5) Å], (VII) [2.59 Å] and (VIII) [2.592 (3) Å]. There are also intra- and intermolecular hydrogen bonds between the nicotinamide N2 and O5 atoms [N2···O5 2.228 (6) Å], and between the non-coordinated O3^i atom of the carboxylate group and the hydroxybenzoate O4 atom [O4···O3^i 2.662 (5) Å; symmetry code: (i) $-1+x, y, z$].

In the carboxylate group, the C7—O2 bond length is a little longer, while the C7—O3 bond length (Table 2) is nearly the same with respect to the corresponding values in complexes (II), (III) and (IV) [(II) 1.251 (1) and 1.253 (2) Å, (III) 1.254 (2) and 1.251 (2) Å, and (IV) 1.251 (6) and 1.254 (7) Å]. On the other hand, the C7—O2 bond length is shorter, while C7—O3 is nearly the same with respect to the values reported in complexes (VII) and (VIII) [(VII) 1.292 (6) and 1.246 (8) Å, and (VIII) 1.283 (4) and 1.254 (5) Å].

The O1—Co—O2 angle [93.4 (1)°] is larger than the corresponding angles in complexes (II), (III) and (IV) [(II) 87.63 (4), (III) 92.67 (6) and (IV) 92.5 (1)°]. On the other hand, the O1—Co—N1 angle (Table 2) is the same as the value reported for complex (IV) [87.9 (2)°], while it is smaller than the value in (III) [92.88 (6)°] and larger than that in complex (II) [86.98 (4)°]. The O2—Co—N1 angle (Table 2) is the same as the corresponding angle in complex (IV) [91.3 (1)°] and larger than that in complexes (II) and (III) [89.36 (4) and 90.19 (6)°, respectively]. The configuration around the Co atom is given by the torsion angles (Table 2). The Co atom is out of the least-squares plane formed by atoms C7, O2 and O3 by 0.582 (4) Å. The dihedral angle between the best planes of the carboxyl group and the phenyl ring in the 3-hydroxybenzoate anion is 14.2 (3)°. The corresponding angles are 13.0 (2), 23.7 (3) and 2.2 (6)° in complexes (II), (III) and (IV), respectively.

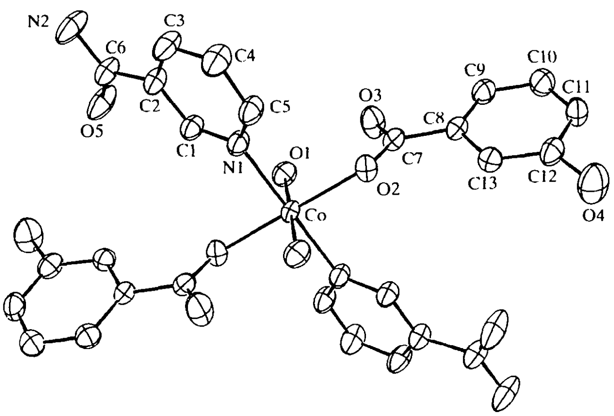


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared from the reaction of $CoSO_4 \cdot 6H_2O$ (0.01 mol) and NA (0.02 mol) in sodium 3-hydroxybenzoate (0.02 mol) solution. The mixture was filtered and set aside to crystallize at ambient temperature for a few days. Suitable pink crystals were obtained.

Crystal data

$[Co(C_7H_5O_3)_2(C_6H_6N_2O)_2\text{-}(H_2O)_2]$
$M_r = 613.45$
Monoclinic
$P2_1/n$
$a = 7.214 (1)$ Å
$b = 18.340 (1)$ Å
$c = 10.418 (1)$ Å
$\beta = 109.32 (1)°$
$V = 1300.7 (2)$ Å^3
$Z = 2$
$D_x = 1.566$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–18°$
$\mu = 0.727$ mm^{-1}
$T = 298$ K
Rod
0.29 × 0.25 × 0.20 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*MolEN*; Fair, 1990)
$T_{min} = 0.810$, $T_{max} = 0.865$
2867 measured reflections
2627 independent reflections

2259 reflections with $F > 3\sigma(F)$
$R_{int} = 0.015$
$\theta_{max} = 26.3°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.075$
$S = 1.29$
2259 reflections
202 parameters
H atoms: see below
$w = 1/[\sigma(F)^2]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co	1/2	0	1/2	0.0248 (2)
O1	0.8046 (5)	0.0265 (2)	0.5786 (3)	0.0366 (2)
O2	0.4136 (5)	0.0978 (2)	0.5682 (3)	0.0331 (2)
O3	0.7070 (5)	0.1472 (2)	0.6676 (4)	0.0494 (2)
O4	0.0127 (6)	0.2176 (3)	0.8378 (4)	0.0621 (1)
O5	0.9245 (5)	−0.0021 (2)	0.1511 (4)	0.0571 (2)
N1	0.4947 (5)	0.0500 (2)	0.3133 (4)	0.0306 (2)
N2	0.8127 (6)	0.0736 (3)	−0.0250 (4)	0.0583 (1)
C1	0.6344 (7)	0.0351 (3)	0.2588 (4)	0.0312 (2)
C2	0.6408 (7)	0.0664 (3)	0.1392 (4)	0.0317 (1)
C3	0.4976 (7)	0.1164 (3)	0.0751 (5)	0.0418 (1)
C4	0.3514 (8)	0.1318 (3)	0.1296 (5)	0.0469 (1)
C5	0.3552 (7)	0.0978 (3)	0.2477 (5)	0.0380 (1)
C6	0.8046 (7)	0.0435 (3)	0.0888 (5)	0.0380 (1)

C7	0.5254 (7)	0.1436 (3)	0.6474 (4)	0.0292 (2)
C8	0.4388 (6)	0.1947 (3)	0.7252 (4)	0.0279 (2)
C9	0.5509 (7)	0.2523 (3)	0.7966 (5)	0.0355 (1)
C10	0.4787 (8)	0.2984 (3)	0.8750 (5)	0.0406 (1)
C11	0.2975 (8)	0.2849 (3)	0.8848 (5)	0.0406 (1)
C12	0.1842 (7)	0.2273 (3)	0.8150 (5)	0.0355 (1)
C13	0.2529 (7)	0.1824 (3)	0.7333 (4)	0.0304 (1)

Table 2. *Selected geometric parameters (Å, °)*

Co—O1	2.132 (3)	O4—C12	1.347 (7)
Co—O2	2.099 (3)	O5—C6	1.224 (6)
Co—N1	2.139 (4)	N1—C1	1.339 (7)
O2—C7	1.263 (5)	N1—C5	1.339 (6)
O3—C7	1.258 (6)	N2—C6	1.327 (7)
O1—Co—O2	93.4 (1)	O4—C12—C11	115.2 (5)
O1—Co—N1	87.6 (1)	O4—C12—C13	124.4 (4)
O2—Co—N1	91.3 (1)	N1—C5—C4	123.0 (5)
Co—O2—C7	126.3 (3)	O5—C6—N2	121.8 (5)
Co—N1—C1	120.6 (3)	N2—C6—C2	117.9 (4)
Co—N1—C5	122.0 (4)	O2—C7—O3	123.3 (5)
O1—Co—O2—C7	−10.3 (4)	O1—Co—N1—C5	−132.6 (4)
N1—Co—O2—C7	−98.0 (4)	O2—Co—N1—C1	139.6 (4)
O1—Co—N1—C1	46.3 (4)	O2—Co—N1—C5	−39.3 (4)

Some of the H-atom positions were determined from difference synthesis and were refined isotropically. The remaining H atoms were positioned geometrically at a distance of 0.95 Å from their parent C atoms and a riding model was used during the refinement process.

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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1329). Services for accessing these data are described at the back of the journal.

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$[Fe(HL)Cl_2]\cdot EtOH$, where H*L* is the monoanion of benzoylacetone *S*-*n*-propylisothiosemicarbazone

Gyula Argay,[a] Alajos Kálmán[a] and Vukadin M. Leovac[b]

[a]*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, PO Box 17, H-1525 Budapest, Hungary, and* [b]*University of Novi Sad, Faculty of Sciences, Institute of Chemistry, Trg D. Obradovica 3, 21000 Novi Sad, Yugoslavia. E-mail: akalman@cric.chemres.hu*

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Abstract

In the title compound, (benzoylacetone *S*-*n*-propylisothiosemicarbazonato-O,N^1,N^4)dichloroiron(III) ethanol solvate, $[Fe(C_{14}H_{18}N_3OS)Cl_2]\cdot C_2H_5OH$, the Fe^{III} ion has a distorted square-pyramidal environment. In the equatorial plane, iron(III) is coordinated by one O and two N atoms from the chelate ligand and by one Cl atom, while the apical position is occupied by the second Cl ligand. The molecule is connected to neighbouring symmetry-equivalent molecules through hydrogen bonds of different types.

Comment

The synthesis of an iron(III) complex with benzoylacetone *S*-methylthiosemicarbazone (H_2L^1) resulting in the formula $[Fe(HL^1)Cl_2]$ has been published previously (Leovac *et al.*, 1994). On the basis of IR spectroscopic and conductometric data, it has been supposed that this complex has a pentacoordinate structure, established by coordinating a monoanion of the tridentate *O*,*N*,*N*-ligand H_2L^1. However, the question as to whether either square-pyramidal (SP) or trigonal-bipyramidal (TBP) coordination occurs remained unanswered. By solving the crystal and molecular structures of a newly synthesized analogous iron(III) complex, (I), having a similar tridentate benzoylacetone *S*-*n*-propylisothiosemicarbazone ligand, the SP configuration of the iron(III) nucleus has been established.