N11—C51^{i}	1.52 (2)	Cl1—O4	1.401 (3)
N2—C2	1.481 (4)	Cl1—O11	1.32 (1)
N2—C3	1.488 (4)	Cl1—O21	1.49 (1)
C1—C2	1.484 (6)	Cl1—O31	1.36 (2)
N1^{i}—Cu1—N1	180.0	N2—C2—C1	108.0 (3)
N11^{i}—Cu1—N11	180.0	N2—C3—C6	111.7 (3)
N1^{i}—Cu1—N2	94.7 (1)	N2—C3—C4	111.0 (3)
N1—Cu1—N2	85.3 (1)	C6—C3—C4	111.8 (3)
N2^{i}—Cu1—N11	91.7 (3)	C7—C4—C3	114.9 (4)
N2—Cu1—N11	88.3 (3)	C7—C4—C51	88.6 (6)
N2^{i}—Cu1—N2	180.0	C3—C4—C51	117.7 (5)
N1—Cu1—O1	88.0 (2)	C7—C4—C5	117.7 (5)
N11—Cu1—O11	85.5 (5)	C3—C4—C5	112.4 (3)
N2—Cu1—O1	82.9 (2)	N1^{i}—C5—C4	112.8 (4)
N2—Cu1—O11	81.8 (5)	N11^{i}—C51—C4	106.3 (10)
O1^{i}—Cu1—O1	180.0	O1—Cl1—O2	106.1 (3)
O11^{i}—Cu1—O11	180.0	O1—Cl1—O3	109.0 (5)
C5^{i}—N1—C1	110.0 (4)	O1—Cl1—O4	114.3 (3)
C5^{i}—N1—Cu1	118.1 (3)	O2—Cl1—O3	107.9 (4)
C1—N1—Cu1	106.4 (3)	O2—Cl1—O4	110.4 (3)
C51^{i}—N11—C1	103.8 (8)	O3—Cl1—O4	108.9 (3)
C51^{i}—N11—Cu1	102.5 (7)	O11—Cl1—O21	106.2 (10)
C1—N11—Cu1	101.3 (5)	O11—Cl1—O31	111 (2)
C2—N2—C3	113.9 (3)	O11—Cl1—O4	108.7 (10)
C2—N2—Cu1	105.4 (2)	O21—Cl1—O31	114.9 (14)
C3—N2—Cu1	116.3 (2)	O21—Cl1—O4	104.7 (7)
C2—C1—N1	104.6 (3)	O31—Cl1—O4	111.4 (11)
C2—C1—N11	119.0 (4)		

Symmetry code: (i) $-x, -y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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trans-Diaquabis(nicotinamide-N^1)bis(4-nitrobenzoato-*O*)cobalt(II)

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Abstract

The title cobalt complex, $[Co(C_7H_4NO_4)_2(C_6H_6N_2O)_2(H_2O)_2]$, is monomeric and centrosymmetric, and contains two water molecules, two 4-nitrobenzoate and two nicotinamide (NA) ligands, all acting as monodentate ligands. The four nearest O atoms around the Co atom form a slightly distorted square-planar arrangement, with a distorted octahedral coordination completed by the pyridine N atoms of the NA ligand, at a distance of 2.134 (2) Å. The water molecules are hydrogen bonded to the carboxyl O atoms [O· · ·O 2.634 (5) Å].

Comment

There are only a few examples of structure determinations of Co^{II} complexes with nicotinic and/or benzoic acid derivatives as ligands, *e.g.* $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2]$ (where DENA is diethylnicotinamide, $C_{10}H_{14}N_2O$; Hökelek & Necefoğlu, 1997), $[Co(CH_3CO_2)_2(DENA)_2(H_2O)_2]$ (Mikelashvili, 1982), $[Co(H_2O)_4(p\text{-}O_2NC_6H_4COO)_2]$ (Nadzhafov *et al.*, 1981) and $[Co(H_2O)_4(p\text{-}H_2NC_6H_4COO)_2]$ (Amiraslanov *et al.*, 1979). The structure–function–coordination relationships of the arylcarboxylate ion in Co^{II} complexes of benzoic acid derivatives change depending on the

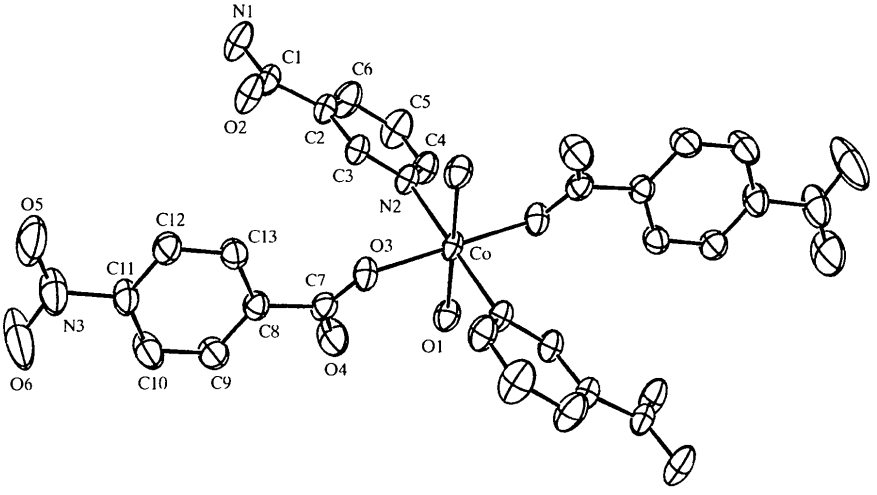
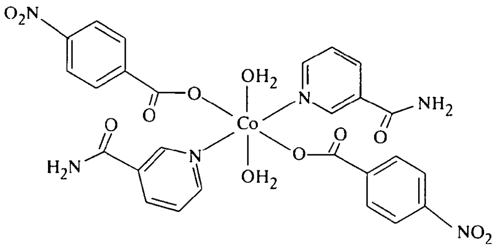


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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; Antsyshkina *et al.*, 1980; Adiwidjaja *et al.*, 1978). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). In the [Co(p-$O_2NC_6H_4COO)_2(H_2O)_4$] complex, Nadzhafov *et al.* (1981) found that the Co atom is situated on a centre of symmetry, and is surrounded by six O atoms forming a slightly distorted octahedron. Four positions are occupied by O atoms from the water molecules, and the other two by the O atoms of the carboxyl groups of the p-nitrobenzoate anions. The structure determination of the title molecule, (I), was undertaken to determine the ligand properties of the nicotinamide (NA) and benzoate ligands, and to compare the coordination geometries when the NA ligands are substituted for water in the Nadzhafov *et al.* (1981) complex. The title compound is a monomeric complex, with Co on a centre of symmetry. All the ligands are monodentate, and the O atoms of each water molecule and benzoate group form a slightly distorted square-planar coordination around the Co atom. The pyridine N atoms of the NA ligand complete a Jahn–Teller-distorted octahedron at distances of 2.134 (2) Å (Fig. 1). There are hydrogen bonds between the carboxyl O4 atoms and water O1 atoms [O4···O1 2.634 (5) Å]. Similar hydrogen bonds are observed in [$Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2$] [O···O 2.687 (5) Å; Hökelek & Necefoğlu, 1997], [$Co(H_2O)_4$(p-$O_2NC_6H_4COO)_2$] [O···O 2.59 Å; Nadzhafov *et al.*, 1981] and [$Co(H_2O)_4$(p-$H_2NC_6H_4COO)_2$] [O···O 2.592 (3) Å; Amiraslanov *et al.*, 1979]. The Co atom lies 0.414 (3) Å out of the C7,O3,O4 least-squares plane. In the carboxylate group, the C7—O3 and C7—O4 bond lengths (Table 1) are the same as in the [$Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2$] complex [1.251 (6) and 1.254 (7) Å; Hökelek & Necefoğlu, 1997], but they are different from the corresponding ones in the [$Co(H_2O)_4$(p-$O_2NC_6H_4COO)_2$] complex [1.292 (6) and 1.246 (8) Å; Nadzhafov *et al.*, 1981]. The dihedral angle between the planar carboxyl group (C7,O3,O4) and the phenyl ring (C8–C13) is 23.7 (3)°. The corresponding angle is 2.2 (6)° in [$Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2$] (Hökelek & Necefoğlu, 1997).



(I)

Experimental

The title compound was prepared from the reaction of $CoSO_4.7H_2O$ (0.01 mol) and NA (0.02 mol) in sodium p-nitrobenzoate solution (0.02 mol). The mixture was filtered and set aside to crystallize at ambient temperature for a few days. Pink crystals suitable for X-ray diffraction were obtained.

Crystal data

[$Co(C_7H_4NO_4)_2(C_6H_6N_2O)_2$-($H_2O)_2$]	Mo $K\alpha$ radiation
M_r = 671.442	λ = 0.71073 Å
Triclinic	Cell parameters from 25 reflections
$P\overline{1}$	θ = 10–18°

$a = 7.5815$ (8) Å
$b = 9.9861$ (9) Å
$c = 10.2413$ (12) Å
$\alpha = 78.417$ (9)°
$\beta = 88.559$ (9)°
$\gamma = 71.491$ (8)°
$V = 719.66$ (14) Å^3
$Z = 1$
$D_x = 1.5493$ Mg m^{-3}
D_m not measured

$\mu = 0.671$ mm^{-1}
$T = 298$ K
Rod
0.30 × 0.25 × 0.25 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.828$, $T_{\max} = 0.846$
3086 measured reflections
2913 independent reflections
2842 reflections with $F > 0$

$R_{\rm int} = 0.064$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections every 250 reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.046$
$S = 1.03$
2842 reflections
205 parameters
H atoms riding
$w = 1/[\sigma(F^2) + (0.02F)^2 + 1]$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co—O1	2.136 (1)	O6—N3	1.199 (3)
Co—O3	2.091 (2)	N1—C1	1.323 (3)
Co—N2	2.134 (2)	N2—C3	1.337 (3)
O2—C1	1.234 (2)	N2—C4	1.335 (2)
O3—C7	1.254 (2)	N3—C11	1.475 (4)
O4—C7	1.251 (2)	C7—C8	1.512 (3)
O5—N3	1.195 (3)		
O1—Co—O3	92.67 (6)	O2—C1—N1	122.2 (2)
O1—Co—N2	92.88 (6)	O2—C1—C2	119.8 (2)
O3—Co—N2	90.19 (6)	N1—C1—C2	118.0 (2)
Co—O3—C7	126.8 (1)	N3—C11—C10	118.5 (2)
Co—N2—C3	119.1 (1)	N3—C11—C12	118.5 (2)
Co—N2—C4	123.0 (4)	N2—C3—C2	123.4 (2)
C3—N2—C4	118.0 (2)	N2—C4—C5	122.4 (2)
O5—N3—O6	122.9 (3)	O3—C7—O4	126.0 (2)
O5—N3—C11	118.8 (2)	O3—C7—C8	117.7 (2)
O6—N3—C11	118.2 (2)	O4—C7—C8	116.3 (2)
O1—Co—O3—C7	−18.3 (2)	O3—Co—N2—C3	34.7 (2)
N2—Co—O3—C7	74.6 (2)	O3—Co—N2—C4	−144.7 (2)
O1—Co—N2—C3	127.4 (2)	Co—O3—C7—O4	14.3 (3)
O1—Co—N2—C4	−52.0 (2)	Co—O3—C7—C8	−162.2 (1)

The title structure was solved by the Patterson method. The H-atom positions were calculated geometrically, with $U_{\rm eq}({\rm H}) = 1.3U_{\rm eq}$ of the parent non-H atom. 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: *SHELXS86* (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: OS1013). Services for accessing these data are described at the back of the journal.

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Bis[μ-methylenebis(dicyclohexylphosphine)-*P*:*P'*]bis[chloropalladium(I)](*Pd*—*Pd*) Diacetonitrile Solvate

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Abstract

A dinuclear palladium(I) complex bridged by two diphosphine ligands, bis[μ-methylenebis(dicyclohexylphosphine)-*P*:*P'*]bis[chloropalladium(I)](*Pd*—*Pd*) diacetonitrile solvate, $[Pd_2Cl_2(C_{25}H_{46}P_2)_2].2C_2H_3N$, has been prepared, and the crystal structure determined.