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trans-Diaquabis(benzoato-*O*)bis(nicotinamide-*N*^{1})cobalt(II)

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Abstract

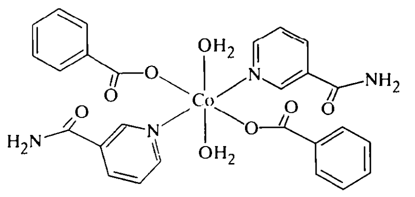
The title compound, $[Co(C_7H_5O_2)_2(C_6H_6N_2O)_2(H_2O)_2]$, is a crystallographically centrosymmetric monomeric complex in which pyridine N, and carboxylate and water O atoms form a tetragonally Jahn–Teller-distorted octahedron about the Co^{II} ion, with bond distances of 2.150 (1), 2.085 (1) and 2.141 (1) Å, respectively. There is a hydrogen bond between nicotinamide N and O atoms [N···O 2.976 (2) Å], and the non-coordinated O atom of the carboxylate group and that of nicotinamide form hydrogen bonds with water O atoms [O···O 2.580 (2) and 2.911 (1) Å, respectively].

Comment

The structures of metal complexes having different benzoic and/or nicotinic acid derivatives as ligands have been the subject of much interest in our laboratory; examples are $[Cu(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(II); where NA is nicotinamide, $C_6H_6N_2O$; Hökelek *et al.*, 1998], $[Cu(C_7H_4NO_4)_2(DENA)_2(H_2O)_2]$ [(III); where DENA is diethylnicotinamide, $C_{10}H_{14}N_2O$; Hökelek *et al.*, 1997], $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2]$ [(IV); Hökelek & Necefoğlu, 1997], $[M(C_7H_4NO_5)_2(H_2O)_4]$ [(V); where M = Zn^{II} and Co^{II}; Tahir *et al.*, 1997], $[Zn_2(C_7H_5O_3)_4(DENA)_2(H_2O)_2]$, [(VI); Hökelek & Necefoğlu, 1996], $[Cu(C_7H_5O_2)_2(DENA)_2]$ [(VII); Hökelek *et al.*, 1996] and $[Cu_2(C_6H_5COO)_4(DENA)_2]$ [(VIII); Hökelek *et al.*, 1995]. The structure–function–coordination relationships of the arylcarboxylate ion in Co^{II} complexes of benzoic acid derivatives change depending 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; Antsyshkina *et al.*, 1980). When pyridine and its derivatives are coordinated instead of water molecules, the structure is completely different (Catterick *et al.*, 1974).

In the $[Co(p\text{-}O_2NC_6H_4COO)_2(H_2O)_4]$ [(IX); Nadzhafov *et al.*, 1981] and $[Co(p\text{-}H_2NC_6H_4COO)_2(H_2O)_4]$ [(X); Amiraslanov *et al.*, 1979] complexes, the Co atoms are situated at centres of symmetry and are surrounded by six O atoms forming slightly distorted octahedrons. Four positions are occupied by water molecules and the other two by O atoms of the carboxyl groups of *p*-nitrobenzoato and *p*-aminobenzoato anions, respectively. In $[Co(C_7H_4NO_4)_2(NA)_2(H_2O)_2]$ [(XI); Hökelek & Necefoğlu, 1998], the Co atom is also situated at a centre of symmetry and is surrounded by four O atoms forming a slightly distorted square-planar arrangement; the pyridine N atoms of NA complete a distorted octahedral coordination.

The structure determination of the title compound, (I), was undertaken in order to determine the ligand properties of nicotinamide (NA) and benzoate ligands, and to compare the coordination geometries when the NA ligands are substituted for water in complexes (IX) and (X). The title compound is a monomeric complex with cobalt in a centre of symmetry. All 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, which is completed to a Jahn-Teller-distorted octahedron by the pyridine N atoms of NA at distances of 2.150 (1) Å (Fig. 1). There are hydrogen bonds (Table 2) between the water O1 atom and the carboxyl O3 and nicotinamide O4 atoms, and between the nicotinamide N2 and O4 atoms. On the other hand, N2—H22 produces an $H22\cdots O3^i$ contact of 2.68 (2) Å, which is too long to be considered as a significant hydrogen bond [symmetry code: (i) $-x$, $-y$, $1-z$]. The $O1\cdots O3^i$ distance (Table 2) is shorter than the corresponding distances in complexes (XI) and (IV) [(XI): O···O 2.634 (5) Å; (IV): O···O 2.687 (5) Å].



(I)

In the carboxylate group, the C1—O2 and C1—O3 bond lengths (Table 1) are the same as in complexes (XI) and (IV) [(XI): 1.251 (2) and 1.254 (2) Å; (IV): 1.251 (6) and 1.254 (7) Å]. On the other hand, the C1—O2 bond length is shorter, while C1—O3 is the same according to the corresponding values in complexes (IX) and (X) [(IX): 1.292 (6) and 1.246 (8) Å; (X): 1.283 (4)

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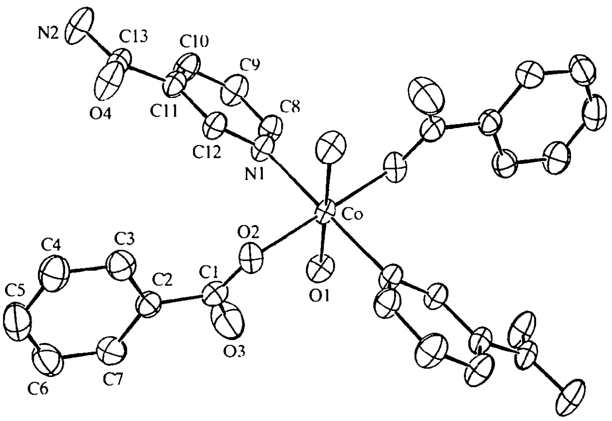

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

and 1.254 (5) Å]. The O1—Co—O2 and O1—Co—N1 angles (Table 1) are smaller than the corresponding angles in complexes (XI) and (IV) [(XI): 92.67 (6) and 92.88 (6)°; (IV): 92.5 (1) and 87.9 (2)°]. The Co atom lies 0.616 (2) Å out of the C1/O2/O3 plane. The dihedral angle between the carboxyl group and the phenyl ring is 13.0 (2)°. The corresponding angles are 23.7 (3) and 2.2 (6)° in complexes (XI) and (IV), respectively.

Experimental

The title compound was prepared from the reaction of $CoSO_4 \cdot 7H_2O$ (0.01 mol) and NA (0.02 mol) in sodium benzoate (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

$[Co(C_7H_5O_2)_2(C_6H_6N_2O)_2(H_2O)_2]$
$M_r = 581.45$
Monoclinic
$P2_1/n$
$a = 7.163 (1)$ Å
$b = 18.299 (1)$ Å
$c = 10.407 (1)$ Å
$\beta = 109.55 (1)°$
$V = 1285.6 (1)$ Å^3
$Z = 2$
$D_x = 1.503$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–18°$
$\mu = 0.757$ mm^{-1}
$T = 298$ K
Rod
0.28 × 0.22 × 0.20 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.809$, $T_{max} = 0.860$
5493 measured reflections
2735 independent reflections

2500 reflections with $F > 0.5\sigma(F)$
$R_{int} = 0.025$
$\theta_{max} = 26.3°$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.038$
$S = 1.38$
2500 reflections
230 parameters
All H-atom parameters refined

$w = 1/[\sigma(I^2) + (0.04F^2)^2]^{1/2}$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ 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	2.141 (1)	O4—C13	1.233 (2)
Co—O2	2.085 (1)	N1—C8	1.342 (2)
Co—N1	2.150 (1)	N1—C12	1.339 (2)
O2—C1	1.255 (1)	N2—C13	1.334 (2)
O3—C1	1.253 (2)		
O1—Co—O2	87.63 (4)	Co—O2—C1	126.23 (9)
O1—Co—N1	86.98 (4)	Co—N1—C8	122.1 (1)
O2—Co—N1	89.36 (4)	Co—N1—C12	120.05 (8)
O1—Co—O2—C1	165.7 (1)	O1—Co—N1—C12	−48.1 (1)
N1—Co—O2—C1	78.6 (1)	O2—Co—N1—C8	−142.2 (1)
O1—Co—N1—C8	130.1 (1)	O2—Co—N1—C12	39.6 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1′···O3^{i}	0.98 (2)	1.64 (2)	2.580 (2)	160 (2)
O1—H2′···O4^{ii}	0.80 (2)	2.16 (2)	2.911 (1)	155 (2)
N2—H21···O4^{iii}	0.84 (2)	2.14 (2)	2.976 (2)	172 (1)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The H-atom positions were determined from difference synthesis and were refined isotropically.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELX*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: NA1389). Services for accessing these data are described at the back of the journal.

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Caesium 5-(2-cyanoethylthio)-2-thioxo-1,3-dithiole-4-thiolate

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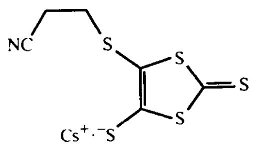
Abstract

The crystal structure of the title compound, $Cs^+\cdot C_6H_4NS_5^-$, (I), shows that the Cs ion is eight-coordinated involving four thiolates, two neutral S atoms and two N atoms. The Cs···S distances are in the range 3.474 (1)–3.810 (1) Å, and the Cs···N distances are 3.317 (5) and 3.389 (5) Å. The three shortest Cs···S distances probably contribute substantially to the unusual stability of (I) in solution and as a solid thiolate stored without special precautions.

Comment

The 2-cyanoethyl group has been used extensively in our group as a versatile protecting group for 1,3-dithiole-4,5-dithiolates and tetrathiafulvalene (TTF) thiolates (Svenstrup *et al.*, 1994). These important building blocks can easily be incorporated into larger assemblies by the effective protection/deprotection methodology. Especially, the mono-deprotection of 2,3-bis(cyanoethylthio)tetrathiafulvalenes and 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thiones (Becher *et al.*, 1994; Simonsen *et al.*, 1996) gives access to a variety of new tetrathiafulvalenes. The thiolates are generated *in situ* in a degassed solution of *N*,*N*-dimethylformamide under an inert atmosphere by addition of a methanolic solution of caesium hydroxide monohydrate. The caesium thiolates, which are stable in solution for at least 24 h, are normally not isolated, but subsequently realkylated with the electrophiles. In the DMIT salt series (DMIT is 2-thioxo-1,3-dithiole-4,5-dithiolate; Svenstrup & Becher, 1995), the van der Waals radius of the counter-ion seems to be the determining factor with regards to stabilization, rather than electronegativity considerations. In contrast to the caesium salts, the sodium and potassium salts have to be isolated using Schlenk techniques. Two stable caesium salts, caesium 5-(methoxycarbonylthio)-2-thioxo-1,3-dithiole-4-thiolate and caesium 3,6,7-tris(methoxycarbonyl)tetrathiafulvalene-2-thiolate, have been isolated and characterized by X-ray crystallography (Lau *et al.*, 1995; Simonsen *et al.*, 1996). In both cases, the neighboring electron-withdrawing methoxycarbonyl group stabilizes the thiolate by delocalization. Furthermore, the carbonyl group is situated in close proximity to the thiolate, resulting in a good bidentate ligand. It was therefore quite interesting that monothiolates bearing a 2-cyanoethylthio group in the α position seem to be very stable in solution and especially that the title compound, (I), is stable as a microcrystalline powder for several months. The present structure determination has been undertaken to throw light on the unusual stability of (I).



(I)

The caesium ion is considered as eight-coordinated, bonding to four S4, one S3, one S5 and two N1 atoms. The Cs···S contact distances are: Cs···S3/S5^{i} 3.810 (1)/3.701 (1) Å and Cs···S4^{ii}/S4^{iii}/S4/S4^{i} 3.474 (1)/3.497 (1)/3.526 (1)/3.762 (1) Å [symmetry codes: (i) $1+x, \frac{3}{2}-y, -\frac{1}{2}+z$; (ii) $1+x, y, z$; (iii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$]. The three shortest Cs···S distances are significantly shorter than the Cs···S distances found in the related compounds caesium 5-methoxycarbonyl-2-thioxo-1,3-dithiole-4-thiolate [Cs···S 3.636 (3) Å; Lau *et al.*, 1995] and caesium-3,6,7-tris(methoxycarbonyl)-tetrathiafulvalene-2-thiolate [Cs···S 3.62 (2) Å; Simonsen *et al.*, 1996]. We think that the three shortest Cs···S contact distances contribute substantially to the stability of (I). The bond-valence parameters (*s*) calculated for these bonds (Brown & Altermatt, 1985) are: Cs···S4^{ii}/S4^{iii}/S4, s = 0.099/0.093/0.086.