

The Crystal Structure of Bis [(*o*-methylbenzoato)(1,3-propanediamine)] nickel (II), [Ni (C₈H₇O₂)₂ (C₃H₁₀N₂)₂]

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The structure of [Ni (C₈H₇O₂)₂ (C₃H₁₀N₂)₂] has been determined from three-dimensional X-ray data and refined by full-matrix least-squares calculations based on *F* to a final *R* value of 0.051 for 1454 reflections. The crystals are orthorhombic, space group *Pbca*, with *a*=10.031(4), *b*=22.540(11), *c*=10.458(3) Å and *Z*=4. The structure is mononuclear with the nickel(II) ion at the centre of the symmetry. Octahedral coordination about Ni is established by the bonds Ni–N1 2.123(5), Ni–N2 2.104(5) and Ni–O1 2.121(4) Å. The 1,3-propanediamine molecule displays a *chair* conformation. The carboxyl group is twisted about 64.5° relative to the benzene ring plane. There is at least one intramolecular and two intermolecular hydrogen bonds involving O2 atom as acceptor and amine nitrogens as donor atoms.

The crystal structure of the title compound has been determined as part of a larger investigation into the monomeric complexes formed by nickel(II) and copper(II) benzoates with 1,3-propanediamine.¹ The studied compound is the first *ortho*-substituted nickel(II) benzoate in this series.

EXPERIMENTAL

Synthesis of the complex. Nickel(II) carbonate (Baker), *o*-methylbenzoic acid (Fluka AG) and 1,3-propanediamine (Fluka AG) in molar ratio 1:2:2 were heated in water-ethanol-2-propanol solution (3:2:1). The blue solution was filtered after 2 d and the filtrate left to dry. The blue

precipitate was collected together with a white precipitate and they were dissolved in an ethanol-2-propanol mixture (3:1) and left to evaporate to dryness. A blue single crystal of approximate dimensions 0.2×0.2×0.35 mm was selected for the X-ray investigation.

Crystallographic work. Lattice parameters were obtained from least-squares refinement of fourteen well-centered reflections measured on a NICOLET P3 diffractometer using graphite monochromatized MoK α radiation ($\lambda=0.7107$ Å). Intensity data were collected ($5^\circ < 2\theta < 55^\circ$) at room temperature using the ω -scan technique and a scan rate varying from 2.0 to 29.3° min⁻¹ depending upon the peak intensity. The intensity of one check reflection measured every 100 reflections showed only statistical fluctuations. Out of 2707 independent reflections measured, 1454 had $F_o > 4\sigma(F_o)$ and were used in the structure determination. The data were corrected for Lorentz and polarization factors but not for absorption nor dispersion. The orthorhombic space group *Pbca* was indicated from the systematic absences. The structure analysis proved this choice to be correct.

CRYSTAL DATA

C₂₂H₃₄NiN₄O₄, *M_r*=477.25Space group: *Pbca**a*=10.031(4), *b*=22.540(11), *c*=10.458(3) Å
V=2364(2) Å³, *F*(000)=1016, *Z*=4 λ (MoK α)=0.7107 Å, μ (MoK α)=0.86 mm⁻¹*D_m*=1.35 g cm⁻³ (flotation), *D_x*=1.341(1) g cm⁻³

Table 1. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	- 696(7)	1083(3)	1712(6)	37(4)
C2	754(7)	1279(3)	1744(7)	39(4)
C3	1542(6)	1157(3)	542(6)	35(3)
C4	979(6)	-1266(3)	3051(6)	34(3)
C5	142(8)	-1322(3)	4091(6)	44(4)
C6	97(11)	-1878(3)	4729(6)	62(5)
C7	884(12)	-2341(3)	4312(10)	82(7)
C8	1718(11)	-2276(4)	3288(10)	78(7)
C9	1755(9)	-1750(3)	2650(8)	59(5)
C10	1090(5)	- 680(3)	2341(6)	30(3)
C11	- 720(8)	- 827(4)	4529(3)	66(5)
N1	- 815(5)	422(2)	1638(5)	32(3)
N2	1731(5)	508(2)	307(4)	32(3)
O1	706(4)	- 691(2)	1198(4)	37(2)
O2	1537(5)	- 243(2)	2911(4)	44(3)
Ni	0	0	0	24(1)

STRUCTURE DETERMINATION

All non-H atomic positions were revealed by Patterson and subsequent electron density calculations. The H atoms were geometrically positioned before the three last cycles by assuming the bond length 1 Å; an isotropic temperature factor $U=0.06 \text{ \AA}^2$ was used. Hydrogen atom parameters were not refined, and the final bond

lengths were between 1.00–1.01 Å. All structure calculations were done using the X-RAY 76 program system and atomic scattering factors of the system.²⁻⁴ Non-H atomic positions and anisotropic thermal parameters were refined by full-matrix least-squares techniques, minimizing the function $\Sigma w(|F_o|-|F_c|)^2$ to the *R* value 0.051 ($R_w=0.062$, unit weights). The residual electron

Table 2. Calculated and unrefined coordinates of the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
H1(C1)	-115	126	93
H2(C1)	-119	123	249
H1(C2)	79	172	193
H2(C2)	121	106	247
H1(C3)	103	133	- 21
H2(C3)	243	136	58
H1(C6)	- 54	-192	548
H1(C7)	84	-273	482
H1(C8)	231	-263	300
H1(C9)	237	-169	187
H1(C11)	- 13	- 48	473
H2(C11)	-132	- 71	379
H3(C11)	-134	- 86	529
H1(N1)	-179	32	169
H2(N1)	- 35	26	242
H1(N2)	233	46	- 46
H2(N2)	221	34	108

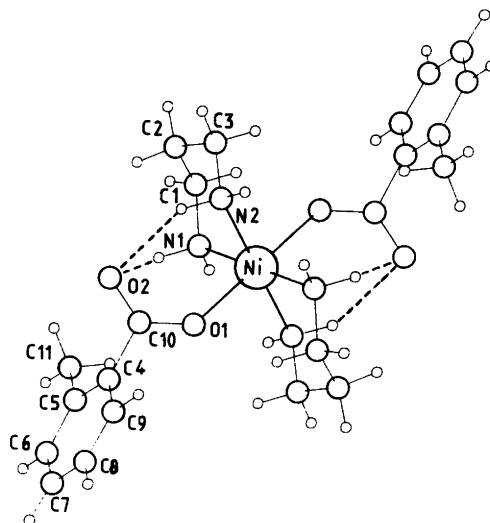


Fig. 1. One centrosymmetric unit of the title compound with labelling of atoms. Intramolecular hydrogen bonds are indicated with broken lines.

Table 3. Bond lengths (Å) and angles (°).

C1–C2	1.520(10)	C4–C10	1.519(9)	C10–O1	1.256(7)
C1–N1	1.497(8)	C5–C6	1.420(10)	C10–O2	1.236(7)
C2–C3	1.511(9)	C5–C11	1.484(12)	N1–Ni	2.123(5)
C3–N2	1.497(8)	C6–C7	1.380(13)	N2–Ni	2.104(5)
C4–C5	1.380(9)	C7–C8	1.367(16)	O1–Ni	2.121(4)
C4–C9	1.405(10)	C8–C9	1.360(12)		
C2–C1–N1	111.5(5)	C4–C5–C11	122.0(6)	C4–C10–O2	119.0(5)
C1–C2–C3	115.4(6)	C6–C5–C11	120.0(7)	O1–C10–O2	125.9(6)
C2–C3–N2	112.3(5)	C5–C6–C7	120.1(8)	C1–N1–Ni	117.2(4)
C5–C4–C9	120.1(6)	C6–C7–C8	121.1(8)	C3–N2–Ni	116.9(4)
C5–C4–C10	120.6(6)	C7–C8–C9	119.6(9)	C10–O1–Ni	130.5(4)
C9–C4–C10	119.3(6)	C4–C9–C8	121.1(8)	N1–Ni–N2	87.2(2)
C4–C5–C6	118.0(7)	C4–C10–O1	115.1(5)	N1–Ni–O1	88.9(2)
				N2–Ni–O1	92.0(2)

density maximum was about $0.41 \text{ e } \text{Å}^{-3}$. Listings of structure factors and anisotropic temperature factors are available from the author.

DISCUSSION

The nickel(II) ion is situated in a centre of symmetry. The nearly regular octahedral stereochemistry is established by the bonds $\text{N1–Ni}=2.123(5)$, $\text{N2–Ni}=2.104(5)$ and $\text{O1–Ni}=2.121(4)$ Å. The O1–Ni bond is tilted $2.3(2)^\circ$ away from the normal to the NiN_4 plane. The N1–Ni–N2 angle is $87.2(2)^\circ$. Ranges in this and the earlier studied nickel(II) benzoates (Ref.

1a) are $2.104(5)–2.158(5)$ Å for coordinated bonds, $2.0–6.7^\circ$ for the tilting of the O1–Ni bond, and $86.3(1)–88.8(1)^\circ$ for the angle N1–Ni–N2 . In accordance with the theoretical calculations of Ceulemans *et al.*⁵, the observed axial O1–Ni distance shows a weak tendency to be longer than the *average* N–Ni bond length.

In the nickel(II) benzoate series the distance C10–O1 is all cases slightly longer than the distance C10–O2 (O2 is uncoordinated). In the title compound C10–O1 is $1.256(7)$ and C10–O2 is $1.236(7)$ Å. The largest C–O bond difference, $0.044(11)$ Å, in the carboxyl group is found in the *meta*-methyl substituted compound, where C10–O1 is $1.278(11)$ and C10–O2 is $1.234(10)$ Å. The observed C–O bond values are between those of single and double bonds.

The twisting of an aromatic carboxyl group (or nitro group) relative to the benzene ring plane usually ranges from a few degrees up to 15 or 20° when there are no *ortho* substituents in the ring. When a large *ortho* substituent is present, the *ipso* carboxyl group may be rotated much more, from 30 to 90° .^{6,7} A twist angle of about 64.5° is found in this study.

The 1,3-propanediamine molecule displays the *chair* conformation, in which the carbon atoms C1 , C2 and C3 are $0.99(1)$, $0.75(1)$ and $0.99(1)$ Å away from the NiN_4 plane. Theoretically estimated values (z -parameters) are 1.05 , 0.75 and 1.05 Å, respectively, when there is an oxygen ligand in an axial position.⁸ According to Gollogly and Hawkins,⁸ 1,3-propanediamine strongly interacts with the axial atoms when in the *chair*

Table 4. The hydrogen bonding networks. The fourth possible H-bond is discussed in the text. Equivalent positions: $i=x+\frac{1}{2}$, y , $-z+\frac{1}{2}$, $j=-x+\frac{1}{2}$, $-y$, $z+\frac{1}{2}$.

$\text{O2}\cdots\text{H2}(\text{N1})$ (Å)	2.27
O2–N1 (Å)	3.10(1)
N1–H2 (Å)	1.01
$\text{O2}\cdots\text{H2–N1}$ (°)	139
$\text{O2}\cdots\text{H1}(\text{N1})^i$ (Å)	2.14
O2–N1^i (Å)	3.09(1)
$\text{N1}^i–\text{H1}^i$ (Å)	1.01
$\text{O2}\cdots\text{H1}^i–\text{N1}^i$ (°)	156
$\text{O2}\cdots\text{H1}(\text{N2})^j$ (Å)	2.11
O2–N2^j (Å)	3.11(1)
$\text{N2}^j–\text{H1}^j$ (Å)	1.01
$\text{O2}\cdots\text{H1}^j–\text{N2}^j$ (°)	172

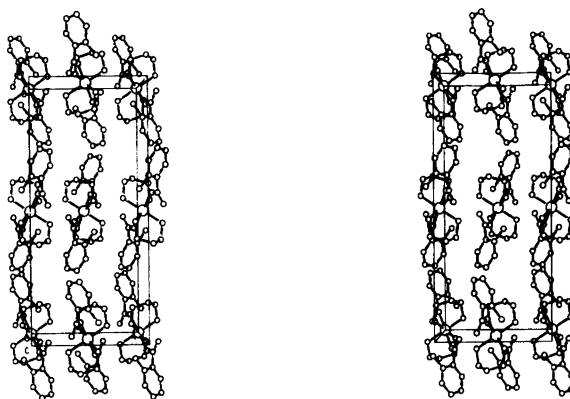


Fig. 2. Stereoscopic view along the c -axis of the unit cell packing.

conformation. In the present compound the distances $N1-O1$ 2.972(7), $N2-O1$ 3.038(7), $N1^i-O1$ 3.030(7), $N2^i-O1$ 2.936(7), $C1^i-O1$ 3.169(8), $C3^i-O1$ 3.082(8), $H1(C3)^i-O1$ 2.48 and $H1(C1)^i-O1$ 2.61 Å are shorter than the sum of the corresponding van der Waals' radii.^{9,10} The superscript i refers to symmetry equivalent atoms at $-x, -y, -z$. The axial oxygen atom clearly interacts with both chelate rings of one centrosymmetric unit. Only minor axial interactions (type H–O), or in some cases no interactions at all, are found in the corresponding copper (II) complexes where the axial bond is about 2.5 Å.^{1b}

The hydrogen bonds form an intra- and intermolecular network. The intermolecular net proceeds along diagonals in the crystallographic $a-c$ plane. A similar planar H-bond network is found in other methyl substituted nickel(II) benzoates.^{1a} The possibility of a fourth hydrogen bond including the O2 atom as the acceptor atom needs to be considered. The fourth, intramolecular bond, has the dimensions $N2-O2$ 3.21(1), $N2-H2$ 1.01 Å, $H2(N2)\cdots O2$ 2.42 Å and the angle $N2-H2\cdots O2$ is 135°. The distance between the hydrogen $H2(N2)$ and oxygen O2 is just slightly over 2.40 Å, which we consider an appropriate upper limit for this kind of interaction. Thus, the bond might possibly be classified as a weak hydrogen bond. As already stated, the H atom positions were fixed with the constant distance 1 Å for N–H bonds (usable for most O–H bonds also). Recently Taylor and Kennard¹¹ have proposed a "normalized" value of 1.030 Å for the N–H distance in N–H \cdots O=C hydrogen bond-

ing systems. The normalizing procedure involves moving the hydrogen atom position along the observed N–H bond direction until the N–H distance is equal to the mean neutron value, 1.030 Å.

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