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[Zn₂(C₃H₅O₂)₄(C₆H₆N₂O)₄] complex. The coordination around each Zn^{II} atom is trigonal bipyramidal. A monodentate propionate anion completes the trigonal basal plane [Zn—O(1) 2.072 (3) Å] and two unidentate nicotinamide ligands occupy the apical positions [Zn—N(11) 2.192 (5) and Zn—N(21) 2.174 (4) Å] of the coordination sphere of each Zn^{II} atom. The Zn···Zn distance is 3.900 (1) Å.

Comment

Complexes where four *syn-syn* carboxylate bridges couple two metal atoms are well known for a wide range of transition metals (Van Niekerk & Schoening, 1953; Mehrotra & Bohra, 1983). In an example of this type of complex containing Zn, [Zn₂(crotonato)₄(quinoline)₂] (Clegg, Little & Straughan, 1986), the metal···metal separation is 2.976 (2) Å, but in [Zn₂(crotonato)₃(crotonato)] (Clegg, Little & Straughan, 1986), which has three *syn-syn* bridges, the Zn···Zn distance is longer at 3.247 (3) Å. Here we report the structure of [Zn(C₆H₆N₂O)₂(μ-C₃H₅O₂)(C₃H₅O₂)₂]₂, (I), which has only two symmetrical *syn-syn* carboxylate bridges and a large Zn···Zn separation of 3.900 (1) Å.

Acta Cryst. (1995). **C51**, 1069–1071

Dimeric Bis(μ-propionato-O:O')-bis[bis(nicotinamide-N)(propionato-O)zinc(II)]

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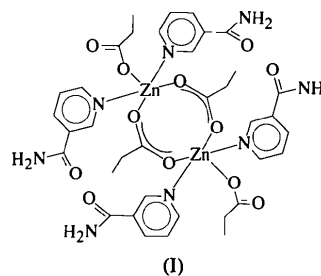
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(Received 16 September 1994; accepted 5 December 1994)

Abstract

Two bidentate-bridging propionate ligands connect two Zn^{II} atoms [Zn—O(3) 2.040 (8) and Zn—O(4)(-x, -y, -z) 2.059 (4) Å] forming a dimeric



The O atoms of the carboxylate ligands form a triangular equatorial plane around each Zn^{II} atom, the nicotinamide ligands being at apical positions (Fig. 1). The distortion from trigonal bipyramidal geometry around each Zn atom is mainly in the equatorial plane, with one of the angles [O(1)—Zn—O(3)] being about 40° more acute than the other two [O(1)—Zn—O(4ⁱ) and O(3)—Zn—O(4ⁱ); symmetry code: (i) -x, -y, -z]. This can be interpreted as a distortion of the coordination geometry towards a square-pyramidal structure whose stability is comparable with that of the trigonal bipyramid. The ends of the propionate skeleton [C(5)—C(6) and C(2)—C(3)] have large displacements, suggesting the possibility of slight disorder. The short C(5)—C(6) distance of 1.430 (23) Å is caused by this disorder.

Hydrogen bonds between the O atom of the carbonyl group and the N atom of the amine group of the nicotinamide ligands link the dimeric molecules into chains in the direction of the *b* axis. These chains are

held together by hydrogen bonds involving the O atoms of unidentate propionate ligands and the N atom of the amine groups.

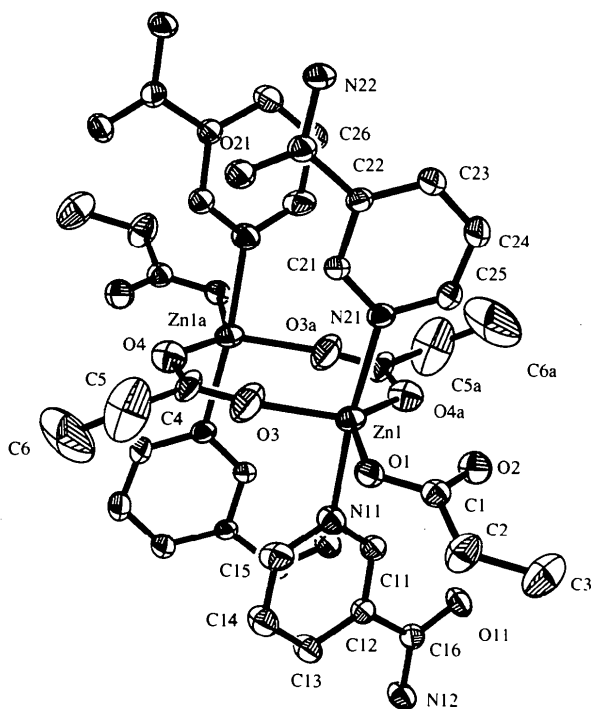


Fig. 1. ORTEP (Johnson, 1965) view of the structure and atomic numbering scheme of the title complex. Displacement ellipsoids are shown at the 35% probability level.

Experimental

The synthesis of the title complex was carried out by the reaction of nicotinamide (0.01 mol) with zinc(II) propionate (0.01 mol) in hot water. Recrystallization was from water.

Crystal data

[Zn₂(C₃H₅O₂)₄(C₆H₆N₂O)₄]

$M_r = 911.55$

Monoclinic

$P2_1/n$

$a = 11.152(3) \text{ \AA}$

$b = 14.767(4) \text{ \AA}$

$c = 12.816(3) \text{ \AA}$

$\beta = 102.560(2)^\circ$

$V = 2060.0(9) \text{ \AA}^3$

$Z = 1$

$D_x = 0.735 \text{ Mg m}^{-3}$

Data collection

Siemens R3m diffractometer
2 θ scans

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 29 reflections

$\theta = 8\text{--}12.5^\circ$

$\mu = 0.629 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.45 \times 0.45 \times 0.20 \text{ mm}$

Colourless

$R_{\text{int}} = 0.0231$

$\theta_{\text{max}} = 27.5^\circ$

Absorption correction:

ψ scan

$T_{\text{min}} = 0.445$, $T_{\text{max}} = 0.602$

5181 measured reflections

4756 independent reflections

2380 observed reflections

$[I > 3\sigma(I)]$

$h = 0 \rightarrow 15$

$k = 0 \rightarrow 20$

$l = -17 \rightarrow 17$

2 standard reflections

monitored every 98

reflections

intensity decay: 3%

Refinement

Refinement on F^2

$R = 0.0499$

$wR = 0.0651$

$S = 1.43$

2380 reflections

262 parameters

H-atom parameters not

refined

$w = 1/[\sigma^2(F) + 0.0010(F)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$

Atomic scattering factors

from SHELXTL-Plus

(Sheldrick, 1990)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
Zn(1)	0.0118 (1)	0.0248 (1)	0.1514 (1)	0.042 (1)
O(1)	0.1086 (3)	0.0171 (2)	0.3085 (3)	0.044 (1)
O(2)	-0.0580 (4)	0.0923 (3)	0.3195 (3)	0.055 (2)
O(3)	0.1377 (7)	-0.0521 (4)	0.0974 (6)	0.132 (4)
O(4)	0.1452 (4)	-0.0880 (3)	-0.0693 (4)	0.060 (2)
O(11)	-0.0547 (3)	0.4032 (3)	0.1170 (3)	0.051 (2)
O(21)	0.0024 (4)	-0.3524 (2)	0.1301 (4)	0.058 (2)
N(11)	0.1112 (4)	0.1508 (3)	0.1386 (4)	0.044 (2)
N(12)	0.1244 (4)	0.4769 (3)	0.1277 (4)	0.051 (2)
N(21)	-0.1042 (4)	-0.0913 (3)	0.1640 (3)	0.038 (2)
N(22)	-0.1801 (4)	-0.4138 (3)	0.1390 (4)	0.051 (2)
C(1)	0.0478 (5)	0.0658 (4)	0.3606 (4)	0.040 (2)
C(2)	0.1114 (7)	0.0923 (5)	0.4726 (5)	0.068 (3)
C(3)	0.0366 (8)	0.1514 (6)	0.5303 (6)	0.094 (4)
C(4)	0.1840 (7)	-0.0839 (4)	0.0283 (6)	0.058 (3)
C(5)	0.3158 (11)	-0.1233 (9)	0.0695 (8)	0.137 (6)
C(6)	0.3991 (11)	-0.1041 (12)	0.0018 (17)	0.175 (12)
C(11)	0.0597 (5)	0.2336 (3)	0.1309 (4)	0.039 (2)
C(12)	0.1265 (5)	0.3129 (3)	0.1328 (4)	0.035 (2)
C(13)	0.2531 (5)	0.3069 (4)	0.1418 (5)	0.049 (2)
C(14)	0.3071 (6)	0.2223 (4)	0.1500 (5)	0.056 (2)
C(15)	0.2345 (6)	0.1468 (4)	0.1492 (5)	0.053 (2)
C(16)	0.0584 (5)	0.4022 (3)	0.1253 (4)	0.038 (2)
C(21)	-0.0748 (5)	-0.1777 (3)	0.1489 (4)	0.036 (2)
C(22)	-0.1498 (5)	-0.2503 (3)	0.1610 (4)	0.035 (2)
C(23)	-0.2597 (5)	-0.2328 (4)	0.1903 (5)	0.050 (2)
C(24)	-0.2907 (6)	-0.1451 (4)	0.2076 (6)	0.059 (3)
C(25)	-0.2134 (5)	-0.0769 (4)	0.1914 (5)	0.051 (2)
C(26)	-0.1039 (5)	-0.3435 (3)	0.1417 (5)	0.040 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Zn(1)—O(1)	2.072 (3)	N(21)—C(21)	1.342 (6)
Zn(1)—O(3)	2.040 (8)	N(11)—C(15)	1.353 (8)
Zn(1)—N(11)	2.192 (5)	N(21)—C(25)	1.356 (8)
Zn(1)—N(21)	2.174 (4)	N(12)—C(16)	1.322 (7)
Zn(1)—O(4 ⁱ)	2.059 (4)	N(22)—C(26)	1.337 (7)
O(1)—C(1)	1.272 (7)	C(11)—C(12)	1.385 (7)
O(3)—C(4)	1.213 (11)	C(21)—C(22)	1.390 (7)
O(2)—C(1)	1.246 (7)	C(12)—C(13)	1.395 (8)
O(4)—C(4)	1.233 (8)	C(22)—C(23)	1.381 (8)
C(1)—C(2)	1.507 (8)	C(12)—C(16)	1.515 (7)
C(4)—C(5)	1.562 (14)	C(22)—C(26)	1.508 (7)
C(2)—C(3)	1.507 (12)	C(13)—C(14)	1.381 (8)
C(5)—C(6)	1.430 (23)	C(23)—C(24)	1.372 (8)
O(11)—C(16)	1.243 (7)	C(14)—C(15)	1.377 (8)
O(21)—C(26)	1.233 (7)	C(24)—C(25)	1.370 (9)
N(11)—C(11)	1.345 (7)		

O(1)—Zn(1)—O(3)	92.7 (2)	N(21)—C(21)—C(22)	123.0 (5)
O(1)—Zn(1)—O(4 ⁱ)	136.6 (2)	C(11)—C(12)—C(13)	118.7 (5)
O(1)—Zn(1)—N(11)	87.3 (2)	C(21)—C(22)—C(23)	118.5 (5)
O(1)—Zn(1)—N(21)	94.4 (2)	C(12)—C(13)—C(14)	118.7 (5)
O(3)—Zn(1)—N(11)	92.9 (2)	C(22)—C(23)—C(24)	119.4 (5)
O(3)—Zn(1)—N(21)	92.9 (2)	C(13)—C(14)—C(15)	119.1 (6)
O(3)—Zn(1)—O(4 ⁱ)	130.6 (2)	C(23)—C(24)—C(25)	118.7 (6)
N(11)—Zn(1)—N(21)	173.8 (2)	N(11)—C(15)—C(14)	123.2 (5)
N(11)—Zn(1)—O(4 ⁱ)	88.0 (2)	N(21)—C(25)—C(24)	123.7 (5)
N(21)—Zn(1)—O(4 ⁱ)	86.7 (2)	C(11)—N(11)—C(15)	117.1 (5)
Zn(1)—O(1)—C(1)	104.8 (3)	C(21)—N(21)—C(25)	116.7 (5)
Zn(1)—O(3)—C(4)	153.8 (6)	Zn(1)—N(11)—C(15)	118.4 (3)
O(1)—C(1)—C(2)	116.9 (5)	Zn(1)—N(21)—C(25)	118.5 (3)
O(3)—C(4)—C(5)	114.6 (7)	C(11)—C(12)—C(16)	118.4 (5)
O(2)—C(1)—C(2)	121.9 (6)	C(21)—C(22)—C(26)	116.8 (5)
O(4)—C(4)—C(5)	114.9 (7)	C(13)—C(12)—C(16)	123.0 (5)
O(1)—C(1)—O(2)	121.2 (5)	C(23)—C(22)—C(26)	124.6 (5)
O(3)—C(4)—O(4)	130.4 (7)	O(11)—C(16)—C(12)	120.0 (5)
C(1)—C(2)—C(3)	114.9 (6)	O(21)—C(26)—C(22)	119.1 (5)
C(4)—C(5)—C(6)	114.1 (10)	O(11)—C(16)—N(12)	122.8 (5)
C(4)—O(4)—Zn(1 ⁱ)	124.6 (5)	O(21)—C(26)—N(22)	122.5 (5)
Zn(1)—N(11)—C(11)	124.2 (4)	N(12)—C(16)—C(12)	117.2 (5)
Zn(1)—N(21)—C(21)	124.8 (4)	N(22)—C(26)—C(22)	118.4 (5)
N(11)—C(11)—C(12)	123.2 (5)		

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

Table 3. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N12—H122 \cdots O21 ⁱ	0.931 (4)	1.957 (4)	2.868 (4)	165.7 (3)
N12—H121 \cdots O1 ⁱⁱ	0.896 (5)	2.145 (5)	2.971 (4)	153.0 (3)
N22—H222 \cdots O2 ⁱⁱⁱ	0.936 (5)	2.156 (5)	3.082 (4)	169.7 (4)
N22—H221 \cdots O11 ^{iv}	0.952 (4)	2.157 (5)	3.085 (5)	164.5 (4)

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

The structure was solved by heavy-atom methods and Fourier techniques, and refined by block-cascade full-matrix least squares with anisotropic displacement factors for all non-H atoms. The H atoms were included at calculated positions with fixed bond lengths ($C-H = 0.96 \text{\AA}$) and constrained angles; displacement parameters were set at 0.080\AA^2 . All calculations were performed with the *SHELXTL-Plus* program package (Sheldrick, 1990), which was also used to produce the figure.

This work was supported by the Slovak Ministry of Education (grant No. 1/990917/93). This financial support is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a stereo packing diagram, have been deposited with the IUCr (Reference: HR1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1071–1073

Azido[2,6-bis(2-benzimidazolyl- N^3)pyridine- N](methanol)(methanolato)nickel(II)

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(Received 5 July 1994; accepted 17 October 1994)

Abstract

The Ni^{II} atom in the title compound, $[Ni(N_3)(CH_3O)(CH_4O)(C_{19}H_{13}N_5)]$, is octahedrally coordinated by three N atoms from the tridentate 2,6-bis(2-benzimidazolyl)pyridine ligand, one N atom from the azide anion and two O atoms from methanol molecules. The four N atoms occupy equatorial positions of the octahedron, with Ni—N bond distances ranging from 2.028 (4) to 2.114 (4) \AA . The methanol O atoms occupy axial positions with Ni—O bond distances of 2.074 (3) and 2.151 (3) \AA .

Comment

Benzimidazole derivatives and their metal complexes have been studied widely since the recognition that many of these materials may serve as models which mimic both the structure and reactivity of metal ion sites in complex biological systems (Sundberg & Martin, 1974; Alagna, Hasnain, Piggott & Williams, 1984). Recently, we have studied metal complexes with