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Structural Investigation of Nickel(II) Complexes. XIII. μ -[2,3,5,6-Tetra-(2-pyridyl)pyrazine]-bis[bis(acetato)aqua-nickel(II)]-Formaldehyde (1/1)

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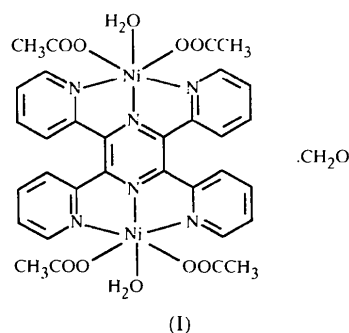
Abstract

In the title compound, $[\text{Ni}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_{24}\text{H}_{16}\text{N}_6)(\text{H}_2\text{O})_2] \cdot \text{CH}_2\text{O}$, the coordination polyhedron of each Ni^{II} centre is a distorted octahedron formed by three N-atom donors from a tetra(2-pyridyl)pyrazine molecule and an aqua O atom in the equatorial positions, and by two O atoms from different acetate anions in the axial positions. The formaldehyde molecule is not coordinated; it

is disordered over two sites related by a crystallographic twofold axis.

Comment

Despite the steric repulsion between its adjacent pyridine rings, the ligand tetra(2-pyridyl)pyrazine (tppz) can act as a bis-tridentate ligand with Cu^{II} (Graf *et al.*, 1993; Valigura *et al.*, 1998), thus forming dinuclear complexes containing two metal atoms bridged by a pyrazine ring. Removal of this steric repulsion was achieved by a twisting deformation of the central pyrazine ring and allowing the Cu^{II} atoms to adopt pentacoordination. Similar deformations of the central pyrazine ring were also found for mononuclear $[\text{Zn}(\text{tppz})\text{Cl}_2]$ (Graf *et al.*, 1993) and $[\text{Cu}(\text{tppz})\text{Cl}_2]$ (Kožišek *et al.*, 1997). We have now extended this work to Ni^{II} complexes and report herein the structure of the title compound, (I).



The crystal structure of the title complex consists of $[\text{Ni}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2(\text{tppz})]$ and CH_2O molecules (Fig. 1) held together by van der Waals interactions and weak intermolecular hydrogen bonds $[\text{O}2 \cdots \text{H}11(-x, 1-y, -z) 2.372 \text{ \AA}]$. The coordination polyhedron of the Ni^{II} atom is a distorted octahedron with nickel-to-donor atom distances within the range 2.001(4)–2.119(4) Å. The greatest deviation from ideal octahedral angles is for $\text{N}1-\text{Ni}1-\text{N}3$ $[156.41(15)^\circ]$ and is attributed to the shape of the tppz ligand. The tendency of the Ni^{II} central atom to adopt the octahedral polyhedron seems to be greater than for Zn^{II} , for which pentacoordinate complexes are found. A *catena*-nickel(II) complex containing pyrazine (Travníček *et al.*, 1996) contains octahedral polyhedra with pyrazine N-atom donors in axial positions and $\text{Ni}-\text{N}$ distances of 2.150(2) Å. On the other hand, the nickel(II) bromide complex with 2,5-dimethylpyrazine (Ayres *et al.*, 1964) exhibits a square-planar configuration with an $\text{Ni}-\text{N}$ distance of 1.85 Å. The anion and/or dianion of 2,3-pyrazinedicarboxylic acid (Mao *et al.*, 1996) gives nickel(II) complexes which are nearly octahedral, with $\text{Ni}-\text{N}$ distances of 2.048(1) and 2.074(1) Å, respectively. The title complex exhibits a similar twisting deformation of the central pyrazine ring, characterized by a dihedral angle of 12.8° between the C–N–C planes.

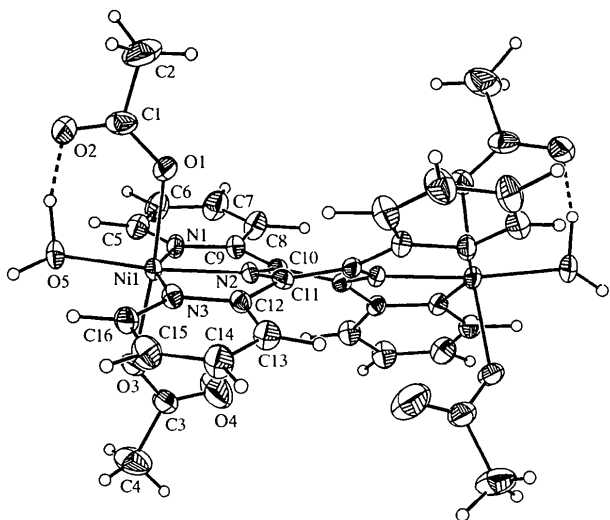


Fig. 1. A view of the structure of [Ni₂(CH₃COO)₄(H₂O)₂(tppez)]. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as spheres of arbitrary radii. The formaldehyde solvent molecule has been omitted for clarity.

The formaldehyde molecule was found not to be coordinated and is disordered over two sites related by a twofold axis. The formaldehyde was probably produced by decomposition of the dimethylformamide used as a crystallization solvent.

A strong intramolecular hydrogen bond was found between atom H16 of the coordinated water molecule and atom O2 of the apical acetate anion (O2···H16 1.43 Å and O2···H16—O5 160°).

Experimental

Nickel(II) acetate tetrahydrate (0.62 g, 2.5 mmol) and tppz (0.19 g, 0.5 mmol) were heated in dimethylformamide (15 ml) under reflux for about 2 h. The yellow–green reaction mixture was filtered and was left in a closed flask at room temperature to crystallize. Yellow–green crystals were obtained.

Crystal data

[Ni₂(C₂H₃O₂)₄(C₂₄H₁₆N₆)-
(H₂O)₂].CH₂O

M_r = 808.08

Monoclinic

C2/c

a = 12.681 (3) Å

b = 12.145 (2) Å

c = 22.107 (4) Å

β = 90.35 (3)°

V = 3404.7 (12) Å³

Z = 4

D_x = 1.576 Mg m⁻³

D_m = 1.58 Mg m⁻³

D_m measured by flotation in
CHBr₃/C₆H₆

Mo *Kα* radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 4.2–12.7°

μ = 1.177 mm⁻¹

T = 293 (2) K

Rectangular prism

0.5 × 0.3 × 0.2 mm

Yellow–green

Data collection

Syntex *P2₁* diffractometer

θ–2θ scans

Absorption correction: none

3864 measured reflections

2773 independent reflections

1758 reflections with

I > 2σ(*I*)

R_{int} = 0.035

θ_{max} = 25.07°

h = –13 → 9

k = –10 → 13

l = –26 → 26

2 standard reflections

every 100 reflections

intensity decay: 15%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.049

wR(*F*²) = 0.169

S = 0.955

2724 reflections

244 parameters

H atoms: shown below

w = 1/[σ²(*F_o*²) + (0.1*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = –0.004

Δρ_{max} = 0.582 e Å⁻³

Δρ_{min} = –0.327 e Å⁻³

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1—N2	2.001 (4)	Ni1—N3	2.100 (4)
Ni1—O5	2.026 (3)	Ni1—N1	2.099 (4)
Ni1—O3	2.051 (4)	Ni1—O1	2.119 (4)
N2—Ni1—O5	173.7 (2)	N2—Ni1—N1	78.0 (2)
N2—Ni1—O3	99.2 (2)	N3—Ni1—N1	156.41 (15)
N2—Ni1—N3	78.4 (2)	N2—Ni1—O1	85.89 (15)

The title structure was solved by Patterson methods. The H atoms (with the exception of those of the water molecules) were included in the refinement at geometrically calculated positions, riding on their parent atoms.

Data collection: *P2₁ Diffractometer Software* (Syntex, 1973). Cell refinement: *P2₁ Diffractometer Software*. Data reduction: *XP21* (Pavelčík, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1200). Services for accessing these data are described at the back of the journal.

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trans-Diaquabis(2-quinolinecarboxylato-N,O)iron(II)–Ethanol–Water (1/2/2)

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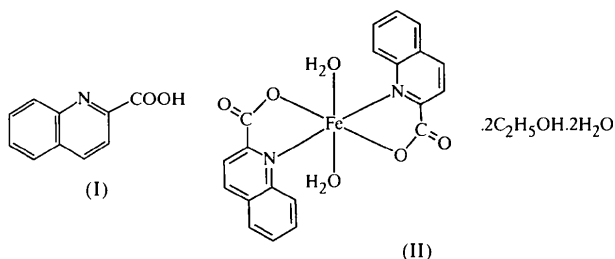
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Abstract

The title compound, $[\text{Fe}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{C}_2\text{H}_6\text{O} \cdot 2\text{H}_2\text{O}$, contains an Fe^{II} ion in a six-coordinate environment. The Fe^{II} ion lies on an inversion centre and displays distorted octahedral geometry with two 2-quinolinecarboxylate and two water ligands in a necessarily *trans* configuration. Complex molecules and uncoordinated water and ethanol molecules are linked together by a hydrogen-bonding network.

Comment

2-Quinolinecarboxylic acid (quinaldinic acid), (I), is one of the final products of tryptophan metabolism (Martin *et al.*, 1983). It is known to be a chelator of transition metal ions (Martell & Smith, 1974). It is converted to kynurenic acid (4-hydroxyquinoline-2-carboxylic acid) by quinaldinic acid 4-monooxygenase, the activity of which is enhanced by Fe^{II} ions (Bubeck *et al.*, 1996). Accordingly, we have undertaken the structure analysis of the chelate compounds of 2-quinolinecarboxylic acid and biologically important Fe^{II} ions in order to clarify the binding scheme of this metabolite to the metal ions. We report herein the structure of the title compound, *trans*-[diaquabis(2-quinolinecarboxylato)iron(II)] diethanol solvate dihydrate, (II). In previous papers, the structures of the Cu^{II} (Haendler, 1986) and Mn^{II} complexes (Haendler, 1996; Okabe & Koizumi, 1997) have been reported.



The molecular structure of the title compound with the atomic labelling is shown in Fig. 1. The title compound contains a six-coordinate Fe^{II} ion with distorted octahedral geometry formed by two 2-quinolinecarboxylate and two water ligands. The six-coordinate geometry found in this study is similar to that found for the Mn^{II} complex of (I) (Haendler, 1996; Okabe & Koizumi, 1997), but different from the pentacoordinate geometry of the Cu^{II} complex (Haendler, 1986). The Fe^{II} ion lies on an inversion centre and is coordinated by two *trans* quinoline N atoms [$\text{Fe}(1)\text{—N}(1)$ 2.270 (1) Å] and by two *trans* carboxylate O atoms [$\text{Fe}(1)\text{—O}(2)$ 2.087 (1) Å] in the equatorial plane, and by two *trans* O atoms of the water molecules in the axial positions [$\text{Fe}(1)\text{—O}(3)$ 2.131 (1) Å]. The carboxy group of the quinoline moiety is ionized and almost coplanar with the quinoline ring plane [$\text{O}(2)\text{—C}(1)\text{—C}(2)\text{—N}(1)$ 3.5 (2)°]. Molecules are connected by hydrogen bonds between the chelated molecules and the solvated water and ethanol molecules (Table 2).

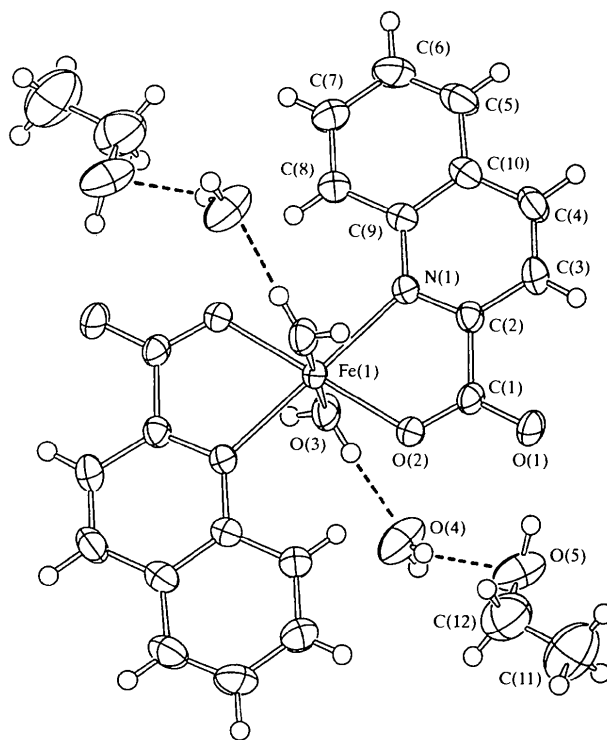


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. Dashed lines indicate hydrogen bonds.

Experimental

The dark-red plate crystal used for analysis was obtained by the slow evaporation of a mixture of 2-quinolinecarboxylic acid and iron(II) sulfate in the molar ratio 4:1 in ethanol solution (ca 90%) at room temperature.