

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 (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N12—H122...O21 ⁱ	0.931 (4)	1.957 (4)	2.868 (4)	165.7 (3)
N12—H121...O1 ⁱⁱ	0.896 (5)	2.145 (5)	2.971 (4)	153.0 (3)
N22—H222...O2 ⁱⁱⁱ	0.936 (5)	2.156 (5)	3.082 (4)	169.7 (4)
N22—H221...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 Å) and constrained angles; displacement parameters were set at 0.080 Å². All calculations were performed with the *SHELXTL-Plus* program package (Sheldrick, 1990), which was also used to produce the figure.

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

PANMING JIAN*

Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

SHUANGXI WANG

Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China

JISHUAN SUO

State Key Laboratory of Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemistry and Physics, Chinese Academy of Science, Lanzhou 730000, People's Republic of China

LIUFANG WANG

National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

QIANGJIN WU

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou Fujian 350002, People's Republic of China

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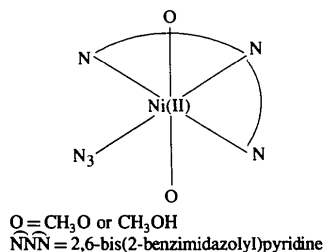
Abstract

The Ni^{II} atom in the title compound, [Ni(N₃)(CH₃O)-(CH₄O)(C₁₉H₁₃N₅)], 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) Å. The methanol O atoms occupy axial positions with Ni—O bond distances of 2.074 (3) and 2.151 (3) Å.

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

2,6-bis(2-benzimidazolyl)pyridine ligands (Wang, Zhu, Zhang, Wang & Wang, 1992; Wang, Luo, Zhou & Zeng, 1993). As an extension of our previous work, we report here the crystal structure of the title complex, (I).



The environment of the Ni atom can be viewed as a distorted octahedron with atoms N(1), N(2) and N(3) from the tridentate ligand and N(11) from the azide ligand in the equatorial plane, while two O atoms [O(21) and O(31)] from two methanol solvent molecules (one deprotonated) occupy the axial positions. Equatorial distances vary between 2.028 (4) and 2.114 (4) Å. With regard to apical distances, the Ni—O(31) distance [2.151 (3) Å] is, as expected, significantly longer than the Ni—O(21) distance [2.074 (3) Å] due to the deprotonation of O(21). The Ni—N(1)(pyridine) distance [2.028 (4) Å] is shorter than the Ni—N(3)(benzimidazole) and Ni—N(2)(benzimidazole) distances [2.114 (4) and 2.061 (4) Å, respectively]. This arrangement is different from that observed in the manganese complex (Wang, Zhu, Zhang, Wang & Wang, 1992), but compatible with the fact that the coordination ability of the pyridine N atom is stronger than that of the benzimidazole N atom. The O(21)—Ni—O(31) angle [178.1(1)°] is close to the ideal value of 180°, while the bond angles in the equatorial plane show greater distortions from the ideal value of 90° [78.0 (1), 77.4 (1), 104.6 (2) and 100.0 (2)° for N(1)—Ni—N(2), N(1)—Ni—N(3), N(2)—Ni—N(11) and N(11)—Ni—N(3), respectively]. These distortions are induced mainly by the steric requirements of the ligand.

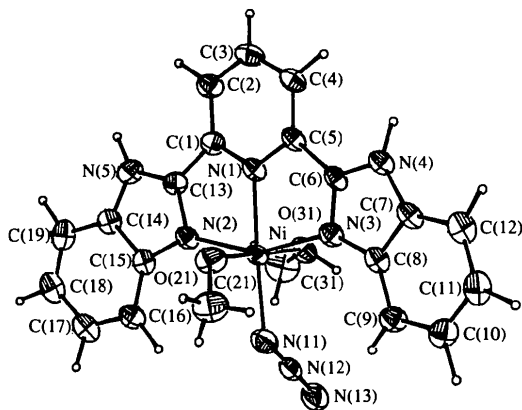


Fig. 1. View of the title compound showing the labelling of the atoms, with 50% probability ellipsoids.

Experimental

The ligand 2,6-bis(2-benzimidazolyl)pyridine (bbp) was synthesized by a previously reported method (Addison & Burke, 1981). Large prismatic blue crystals of the title complex were obtained by slow evaporation of a solution of Ni(bbp)Cl₂·H₂O and excess NaN₃ in methanol. Green Ni(bbp)Cl₂·H₂O was prepared by addition of stoichiometric amounts of NiCl₂·6H₂O to bbp in methanol solution with stirring.

Crystal data

[Ni(N₃)(CH₃O)(CH₄O)-
(C₁₉H₁₃N₅)]

M_r = 475.14

Monoclinic

*P*2₁/*n*

a = 9.668 (2) Å

b = 8.358 (2) Å

c = 25.582 (9) Å

β = 98.26 (3)°

V = 2046 (2) Å³

Z = 4

D_x = 1.54 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 14.16–14.90°

μ = 0.987 mm⁻¹

T = 289 K

Prism

0.4 × 0.3 × 0.1 mm

Blue

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

empirical

T_{min} = 0.896, *T_{max}* =

1.000

4010 measured reflections

3944 independent reflections

2715 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.036

θ_{max} = 25°

h = -11 → 11

k = 0 → 9

l = 0 → 30

3 standard reflections

frequency: 60 min

intensity decay: 2.6%

Refinement

Refinement on *F*

R = 0.051

wR = 0.065

S = 1.75

2715 reflections

289 parameters

H-atom parameters not

refined

w = 1/σ²(*F_o*)

(Δ/σ)_{max} = 0.04

Δρ_{max} = 0.61 e Å⁻³

Δρ_{min} = -0.56 e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Ni	0.16473 (6)	0.08652 (7)	0.87788 (2)	2.12 (3)
O(21)	0.2087 (4)	0.2916 (4)	0.8377 (1)	3.4 (2)
O(31)	0.1234 (3)	-0.1230 (4)	0.9219 (1)	3.1 (2)
N(1)	0.3355 (4)	-0.0205 (5)	0.8558 (1)	2.2 (2)
N(2)	0.0825 (4)	-0.0225 (5)	0.8080 (1)	2.4 (2)
N(3)	0.3247 (4)	0.1499 (5)	0.9397 (1)	2.4 (2)
N(4)	0.5555 (4)	0.1536 (5)	0.9663 (1)	2.4 (2)
N(5)	0.1301 (4)	-0.1680 (5)	0.7376 (2)	2.8 (2)
N(11)	-0.0038 (4)	0.1967 (5)	0.9039 (2)	3.3 (2)
N(12)	-0.0747 (4)	0.1590 (5)	0.9349 (1)	2.7 (2)
N(13)	-0.1479 (4)	0.1231 (7)	0.9658 (2)	4.3 (2)

C(1)	0.3211 (5)	-0.1079 (6)	0.8114 (2)	2.4 (2)
C(2)	0.4357 (5)	-0.1862 (6)	0.7957 (2)	3.1 (2)
C(3)	0.5633 (5)	-0.1674 (7)	0.8265 (2)	3.1 (2)
C(4)	0.5793 (5)	-0.0738 (6)	0.8716 (2)	2.8 (2)
C(5)	0.4602 (5)	-0.0022 (6)	0.8853 (2)	2.3 (2)
C(6)	0.4492 (5)	0.0996 (6)	0.9310 (2)	2.3 (2)
C(7)	0.4965 (5)	0.2507 (6)	1.0015 (2)	2.4 (2)
C(8)	0.3518 (5)	0.2476 (6)	0.9841 (2)	2.5 (2)
C(9)	0.2606 (5)	0.3363 (7)	1.0105 (2)	3.0 (2)
C(10)	0.3201 (6)	0.4249 (6)	1.0535 (2)	3.4 (2)
C(11)	0.4648 (6)	0.4264 (6)	1.0702 (2)	3.3 (2)
C(12)	0.5555 (5)	0.3383 (6)	1.0453 (2)	3.0 (2)
C(13)	0.1773 (5)	-0.1055 (6)	0.7844 (2)	2.4 (2)
C(14)	-0.0076 (5)	-0.1235 (6)	0.7283 (2)	2.5 (2)
C(15)	-0.0371 (5)	-0.0329 (6)	0.7719 (2)	2.4 (2)
C(16)	-0.1698 (5)	0.0335 (6)	0.7731 (2)	3.0 (2)
C(17)	-0.2694 (5)	0.0076 (7)	0.7298 (2)	3.2 (2)
C(18)	-0.2399 (5)	-0.0816 (7)	0.6863 (2)	3.4 (2)
C(19)	-0.1106 (6)	-0.1480 (7)	0.6851 (2)	3.2 (2)
C(21)	0.1714 (6)	0.4478 (7)	0.8479 (2)	4.3 (3)
C(31)	0.0043 (7)	-0.2211 (8)	0.9064 (3)	4.8 (3)

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

Ni—N(1)	2.028 (4)	Ni—O(21)	2.074 (3)
Ni—N(2)	2.061 (4)	Ni—N(3)	2.114 (4)
Ni—N(11)	2.063 (4)	Ni—O(31)	2.151 (3)
N(1)—Ni—N(2)	78.0 (1)	N(2)—Ni—O(31)	91.0 (1)
N(1)—Ni—N(11)	177.3 (2)	N(11)—Ni—O(21)	91.0 (2)
N(1)—Ni—O(21)	89.6 (1)	N(11)—Ni—N(3)	100.0 (2)
N(1)—Ni—N(3)	77.4 (1)	N(11)—Ni—O(31)	88.9 (2)
N(1)—Ni—O(31)	90.4 (1)	O(21)—Ni—N(3)	89.1 (2)
N(2)—Ni—N(11)	104.6 (2)	O(21)—Ni—O(31)	178.1 (1)
N(2)—Ni—O(21)	90.9 (2)	N(3)—Ni—O(31)	89.1 (1)
N(2)—Ni—N(3)	155.3 (1)	N(12)—N(11)—Ni	131.9 (4)

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983) and refined by full-matrix least-squares methods. All non-H atoms were located in successive $\Delta\rho$ maps and refined with anisotropic displacement parameters. All H atoms were located geometrically and included with isotropic displacement parameters in the structure-factor calculations, but not refined.

This research was supported by grants from the National Natural Science Foundation of China and the Fuzhou State Key Laboratory of Structure Chemistry.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: AB1196). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethylenediaminium Dichromate

PABLO A. LORENZO-LUIS, PEDRO MARTÍN-ZARZA AND PEDRO GILI*

Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de La Laguna, 38200 La Laguna Tenerife, Canary Islands, Spain

JUAN M. ARRIETA

Departamento de Química Inorgánica, Universidad del País Vasco, Apdo 644, Bilbao, Spain

GABRIEL GERMAIN

Unité de Chimie Physique Moléculaire et de la Cristallographie, Université de Louvain, Place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

LEON DUPONT

Laboratoire de Cristallographie, Institut de Physique B5, Université de Liege au Sart-Tilman, B-4000 Leige, Belgium

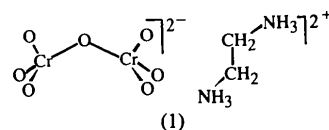
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Abstract

The synthesis, characterization, and crystal and molecular structures of $\text{C}_2\text{H}_{10}\text{N}_2^{2+}\cdot\text{Cr}_2\text{O}_7^{2-}$ are described. The structure of this compound was determined by X-ray crystallography and showed that the $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$ organic cations are bound to the $\text{Cr}_2\text{O}_7^{2-}$ anions by N—H...O hydrogen-bonding interactions [2.988 (3) \AA and 92.30 (17) $^\circ$].

Comment

To our knowledge, no fluoropolychromates(VI) have been reported previously. We attempted to prepare an organic fluoropolychromate(VI) from organic base, chromium(VI) trioxide and HF in aqueous medium, but obtained instead an organic dichromate(VI). We describe here the preparation, characterization, and molecular and crystal structures of ethylenediaminium dichromate, (1).



A view of the molecule is shown in Fig. 1, with the unit-cell packing in Fig. 2. The structure consists of discrete dinegative dichromate anions hydrogen bonded to