

cis-Aquabis(2,2'-bipyridine-*N,N'*)[dichromato(2-)-O¹]nickel(II)

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.029

w*R* factor = 0.075

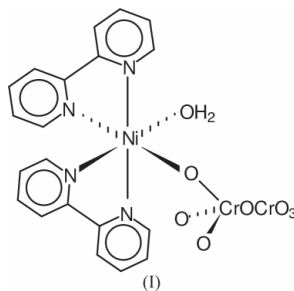
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecular structure of the title compound, $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})\{\text{Cr}_2\text{O}_7\}]$, contains an Ni^{II} atom with a distorted *cis*-octahedral coordination formed by two chelating bipyridine (bipy) ligands [mean Ni–N_{bipy} = 2.068 (3) Å], one water molecule [Ni–O = 2.086 (3) Å] and an O atom of the dichromate anion [Ni–O = 2.083 (2) Å]. One of the water H atoms is involved in the intramolecular hydrogen bond with the terminal O atom of the dichromate ligand [O···O 2.743 (5) Å], whereas its second H atom participates in the intermolecular hydrogen bonding [O···O 2.688 (4) Å]; the latter is responsible for the formation of the infinite chains stretching along the polar *c* axis of the crystal.

Comment

The industrial importance of chromium(VI) compounds, together with their toxic and genotoxic character, are the reasons for considerable attention attracted by the studies of the metal complexes containing compounds of chromium(VI) as ligands (Dave & Czernuszewicz, 1994). In particular, a coordination model based on the study of chromates and dichromate complexes of transition metals with organic ligands, has been proposed to explain the decrease in the mutagenic activities of the chromium(VI) compounds (Gili & Lorenzo-Luis, 1999).



Many transition metal complexes containing $[\text{Cr}_2\text{O}_7]^{2-}$ and organic bases as ligands have been structurally characterized (Ugglá *et al.*, 1970; Jameson *et al.*, 1986; Munno *et al.*, 1998; Pan *et al.*, 1998) because of their special properties in such areas as analytical chemistry, catalysis and magneto-chemistry.

In our current research on dichromate complexes of transition metals with magnetic properties, we have prepared a new nickel(II) dichromate with bipy as chelating ligand (Fig. 1). The asymmetric unit of the title complex, (I), involves an Ni^{II} atom with a distorted octahedral coordination environment provided by a pair of chelating bipy ligands, water molecule and O atom of the Cr_2O_7 group, oxygen ligands occupying *cis* positions in the octahedron. The Ni–N_{bipy} bond

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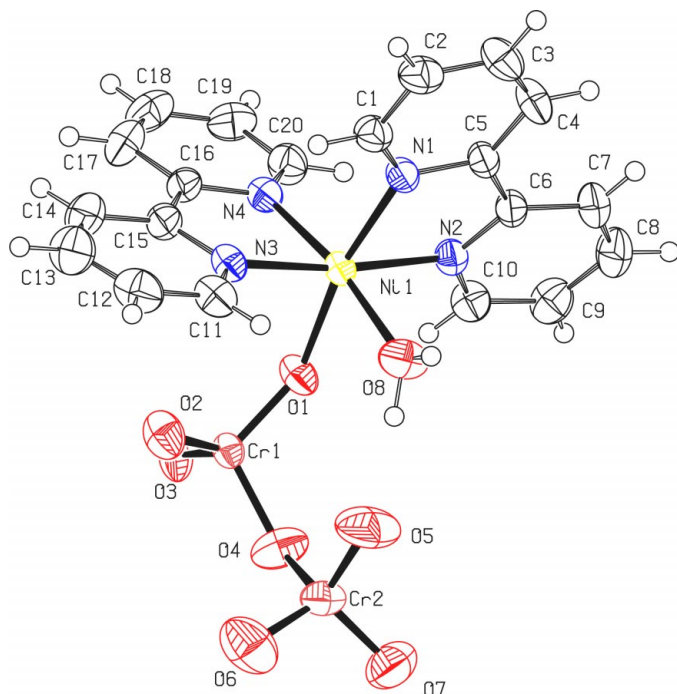


Figure 1
A perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

distances [mean value 2.068 (3) Å] are slightly shorter than the Ni–O_{water} bond length [2.086 (3) Å]. The N–Ni–N bite angles [79.04 (12) and 79.21 (12)°] agree well with those reported previously for other nickel(II) complexes containing bipy (Wada *et al.*, 1976; Cortés *et al.*, 1994; Román *et al.*, 1995; Hernández-Molina *et al.*, 1999). As expected, both bipy ligands are nearly planar [the largest deviation from their mean planes is 0.069 (4) Å for C10], the certain degree of twisting of the pyridyl rings in the bipy ligands relative to each other [in the title compound, the twist angles are 5.1 (2) and 2.1 (2)° for N1/N2/C1–C10 and N3/N4/C11–C20, respectively] is perfectly normal; angles up to 18° have been observed previously (Cano *et al.*, 1994). The mean planes of the two bipy molecules are inclined by 71.67 (10)° with respect to one another.

Each Cr atom in (I) exhibits a slightly distorted tetrahedral geometry. The two tetrahedral CrO₄ groups share one O atom (O4) thus forming a dichromate anion in an almost eclipsed conformation. The Cr–O–Cr bridging angle is 129.2 (2)°, a value which is in the range of previously reported dichromate-containing compounds (Mestres *et al.*, 1993; Martín-Zarza *et al.*, 1995). The bridging Cr–O bonds are 1.744 (3) and 1.812 (3) Å for Cr1–O4 and Cr2–O4, respectively. They are longer than the terminal Cr–O bonds, the maximum and minimum bond lengths for the latter being 1.640 (3) (Cr1–O3) and 1.580 (3) Å (Cr1–O2). The O–Cr–O bond angle range is 104.9 (2)–111.8 (2)° and Cr–O–Ni bridging angle [140.73 (14)°] is in accordance with the analogous parameters in similar compounds (Oshio *et al.*, 1997; Ki-Young *et al.*, 1999).

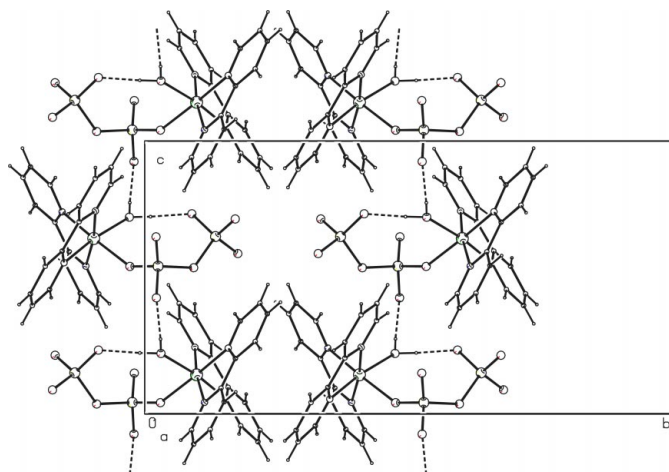


Figure 2
The molecular packing of the complex showing intra- and intermolecular hydrogen bonds.

The water molecule coordinated to the Ni^{II} atom forms one intramolecular hydrogen bond with the terminal O atom of the dichromate ligand [O8··O5 2.743 (5) Å], as well as one intermolecular hydrogen bond [O8··O3ⁱ 2.688 (4) Å; symmetry code: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$] (Fig. 2). The latter hydrogen bond links the molecules of the complex into the infinite chains stretching along the *c* axis of the crystal.

Experimental

Prismatic brown single crystals of the title compound were grown by a slow diffusion. Into one arm of the H-double-tube glass vessel were added K₂Cr₂O₇ (10 ml, 0.1 M water solution) and NiCl₂·6H₂O (10 ml, 0.1 M water solution). Into the other arm 2,2'-bipy was added (20 ml, 0.1 M in acetone). Both arms were covered by acetone and protected by parafilm to avoid acetone evaporation. The vessel was allowed to stand at room temperature. A few crystals of the compound appeared after one month. The crystals were selected and washed with some drops of cold water–ethanol (1:1) solution.

Crystal data

[NiCr₂O₇(C₁₀H₈N₂)₂(H₂O)]
M_r = 605.07
 Orthorhombic, *Fdd*2
a = 33.958 (5) Å
b = 22.880 (3) Å
c = 11.7350 (10) Å
V = 9118 (2) Å³
Z = 16
D_x = 1.763 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 12.0–18.2°
 μ = 1.81 mm⁻¹
T = 293 (2) K
 Prism, brown
 0.45 × 0.23 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.613, *T_{max}* = 0.762
 3459 measured reflections
 3459 independent reflections

2927 reflections with *I* > 2σ(*I*)
 θ_{\max} = 30.0°
h = 0 → 47
k = 0 → 32
l = -16 → 0
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.7783P]$
$R(F) = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.08$	$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
3459 reflections	$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$
316 parameters	Absolute structure: (Flack, 1983), no Friedel pairs
H-atom parameters constrained	Flack parameter = 0.07 (2)

Table 1
Selected geometric parameters (\AA , $^\circ$).

Ni1—O1	2.083 (2)	Cr1—O2	1.580 (3)
Ni1—O8	2.086 (3)	Cr1—O3	1.640 (3)
Ni1—N1	2.054 (3)	Cr1—O4	1.744 (3)
Ni1—N2	2.081 (3)	Cr2—O4	1.812 (3)
Ni1—N3	2.057 (3)	Cr2—O5	1.596 (4)
Ni1—N4	2.083 (3)	Cr2—O6	1.589 (4)
Cr1—O1	1.629 (3)	Cr2—O7	1.601 (4)
O1—Ni1—N1	169.26 (10)	Ni1—O1—Cr1	140.73 (14)
O8—Ni1—N4	170.57 (12)	Cr1—O4—Cr2	129.2 (2)
N2—Ni1—N3	172.58 (11)		

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H81 \cdots O5	0.93	1.82	2.743 (5)	175
O8—H82 \cdots O3 ⁱ	0.77	1.93	2.688 (4)	165

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

All H atoms have been generated at idealized geometries, except for those belonging to the water molecule which were located in difference syntheses, and refined isotropically using a riding model with displacement parameters set at $1.2U_{\text{eq}}$. The residual electron-density maximum is 0.47 \AA^{-3} from the Ni1 atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*,

1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON*.

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