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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.058

wR factor = 0.142

Data-to-parameter ratio = 12.4

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

Tris(2,2'-bipyridine)nickel(II) diperchlorate

The title compound, $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2$, is built up of monomeric $[\text{Ni}(\text{bpy})_3]^{2+}$ cations (bpy = 2,2'-bipyridine) and two perchlorate anions. The asymmetric unit is one half cation and one anion, a twofold rotation axis passing through the Ni atom and bisecting one bpy ligand. The Ni^{II} ion is coordinated by six N atoms from three chelating bpy ligands in a highly distorted octahedral geometry, with Ni–N bond lengths ranging from 2.071 (4) to 2.091 (4) Å.

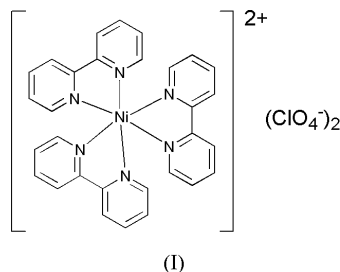
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Comment

When trying to prepare the nickel(II) complex containing 2,2'-bipyridine and 1,3,5-benzenetricarboxylate ligands by hydrothermal reaction, we did not obtain the expected compound but, instead, red prismatic crystals of tris(2,2'-bipyridine)-nickel(II) diperchlorate, (I), grew from the above solution on slow evaporation. The new complex has been characterized by elemental analysis and single-crystal diffraction analysis.



The title compound crystallizes in space group $C2/c$ and consists of monomeric $[\text{Ni}(\text{bpy})_3]^{2+}$ cations and perchlorate anions, being isostructural with the zinc(II) complex (Chen *et al.*, 1995*a,b*). The asymmetric unit is one half cation and one anion, a twofold rotation axis passing through the Ni atom and bisecting one bpy ligand. The nickel(II) ion is coordinated by six N atoms from three chelating bpy ligands in a highly distorted octahedral geometry (Fig. 1), with Ni–N bond lengths ranging from 2.071 (4) to 2.091 (4) Å, shorter than those [2.135 (2)–2.172 (3) Å] of the isomorphous Zn^{II} compound; this may be attributed to the smaller ionic radius of the Ni^{2+} cation. As in the Zn^{II} isomorph, each pair of pyridine rings in the three bpy ligands are non-coplanar, with a dihedral angle between each pair ranging from *ca* 7.2 to 18.3°, larger than in the Zn^{II} isomorph. The distorted N–Mn–N angles resulting from the chelating bpy ligands range from 78.6 (1) to 79.1 (2)°, larger than those of the Zn^{II} isomorph [75.8 (1)–77.2 (1)°]. The crystal structure of the title compound is composed of two-dimensional layers parallel to the *ab* plane. The molecular packing reveals the occurrence of pillars of cations and anions parallel to the *c* axis (Fig. 2).

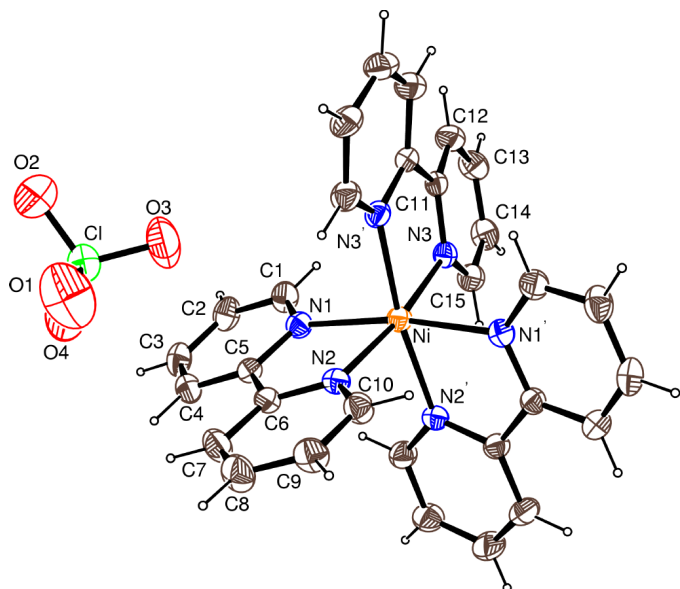


Figure 1

View of the cation and anion of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The hydrothermal reaction of nickel perchlorate (0.06 g, *ca* 0.20 mmol), 2,2'-bipyridine (0.05 g, 0.32 mmol) and 1,3,5-benzenetricarboxylic acid (0.05 g, 0.24 mmol) in a molar ratio of *ca* 2:3:2, at 433 K for 4 d, gave, after cooling to room temperature at 5 K h⁻¹, a pale green solution. Red prismatic crystals of [Ni(bpy)₃](ClO₄)₂ were grown from the solution by slow evaporation for about four days, and isolated in 54% yield (based on Ni). Elemental analysis calculated for C₃₀H₂₄Cl₂N₆NiO₈: C 49.62, H 3.33, N 11.57%; found: C 49.51, H 3.10, N 11.39%.

Crystal data

[Ni(C₁₀H₈N₂)₃](ClO₄)₂
M_r = 726.16
 Monoclinic, *C*2/*c*
a = 17.502 (2) Å
b = 10.777 (1) Å
c = 16.092 (2) Å
 β = 90.959 (2)°
V = 3034.8 (6) Å³
Z = 4

D_x = 1.589 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2134 reflections
 θ = 2.2–25.0°
 μ = 0.88 mm⁻¹
T = 293 (2) K
 Prism, red
 0.46 × 0.34 × 0.26 mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.621, *T_{max}* = 0.796
 4475 measured reflections

2637 independent reflections
 2026 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 25.0°
h = -20 → 12
k = -12 → 8
l = -19 → 19

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.058
wR (*F*²) = 0.142
S = 1.08
 2637 reflections
 213 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 12.8239P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.40 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.37 \text{ e } \text{Å}^{-3}$

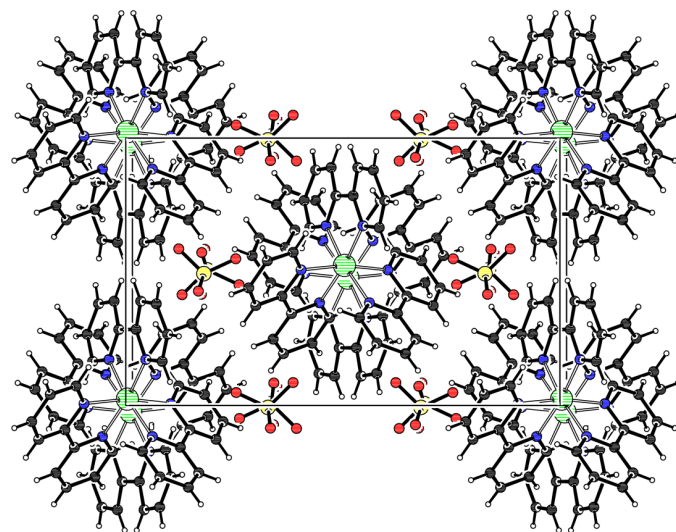


Figure 2

Packing of the title complex, viewed along the *c* axis. H atoms have been omitted for clarity.

Table 1

Selected geometric parameters (Å, °).

Ni—N3	2.071 (3)	Cl—N1	1.342 (6)
Ni—N2	2.085 (3)	C5—N1	1.348 (5)
Ni—N1	2.090 (3)	C6—N2	1.345 (5)
Cl—O4	1.373 (4)	C10—N2	1.343 (6)
Cl—O1	1.381 (5)	C11—N3	1.347 (5)
Cl—O3	1.417 (4)	C15—N3	1.350 (6)
Cl—O2	1.429 (5)		
N3—Ni—N3 ⁱ	79.1 (2)	N3 ⁱ —Ni—N1	93.0 (1)
N3—Ni—N2	172.1 (1)	N2—Ni—N1	78.5 (1)
N3 ⁱ —Ni—N2	97.1 (1)	N2 ⁱ —Ni—N1	94.2 (1)
N2—Ni—N2 ⁱ	87.5 (2)	N1—Ni—N1 ⁱ	170.1 (2)
N3—Ni—N1	94.7 (1)		

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

All H atoms were located in a difference Fourier map but were introduced in idealized positions and treated as riding. All H atoms were located in a difference Fourier map but were introduced in idealized positions (C—H = 0.93 Å) and treated as riding, with displacement parameters fixed at 120% of those of their parent atoms.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1994); program(s) used to solve structure: SHELXTL (Siemens, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLUTON (Spek, 2003) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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References

Chen, X., Wang, R. & Yu, X. (1995a). *Acta Cryst.* **C51**, 1545–1547.

Chen, X., Wang, R. & Xu Z. (1995*b*). *Acta Cryst.* **C51**, 820–822.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. Release 97-2). University of Göttingen, Germany.

Siemens (1994). *SAINTE* and *SHELXTL* (Version 5). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.