Bis(2,2'-bipyridine-κ^2N,N')(croconato-κ^2O,O')nickel(II)

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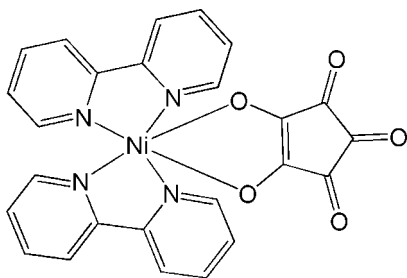
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The title compound, [Ni(C_5O_5)($C_{10}H_8N_2$)$_2$], lies across a crystallographic twofold axis, around which two 2,2'-bipyridine (2,2'-bipy) ligands are arranged in a propeller manner. The local geometry of the NiN_4O_2 coordination core basically adopts an octahedral geometry. The molecular twofold axis is along the direction of the molecular dipole moment, and the complex is packed with its dipole moment alternately along the $+b$ and $-b$ directions. The crystal structure is stabilized by intermolecular C—H···O hydrogen bonds.

Related literature

For the synthesis, see: Chen *et al.* (2008). For related structures, see: Chen *et al.* (2005, 2007). For other related literature, see: Coronado *et al.* (2007); Wang *et al.* (2002).

Experimental

Crystal data

[Ni(C_5O_5)($C_{10}H_8N_2$)$_2$]
$M_r = 511.13$
Orthorhombic, $Pbcn$
$a = 12.725$ (5) Å
$b = 10.752$ (5) Å
$c = 15.733$ (5) Å
$V = 2152.6$ (15) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.95$ mm^{-1}
$T = 293$ (2) K
$0.20 \times 0.19 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{min} = 0.821$, $T_{max} = 0.902$
10055 measured reflections
2466 independent reflections
1536 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.102$
$S = 1.02$
2466 reflections
160 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1^i	0.93	2.57	3.340 (4)	141
C8—H8···O2^{ii}	0.93	2.24	3.114 (4)	156
C9—H9···O3^{iii}	0.93	2.57	3.222 (4)	127

Symmetry codes: (i) $x, -y+1, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2071).

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supplementary materials

Bis(2,2'-bipyridine-κ^2N,N')(croconato-κ^2O,O')nickel(II)

H.-F. Chen, Q. Fang and W.-T. Yu

Comment

The croconate $C_5O_5{}^{2-}$ anion has attracted increasing attention in recent years because this polydentate ligand gave rise to a variety of interesting complexes (Chen *et al.*, 2008; Coronado *et al.*, 2007; Chen *et al.*, 2005; Wang *et al.*, 2002;). Typically, the $C_5O_5{}^{2-}$ anion serves as a terminal bidentate chelate ligand or a bridging ligand utilizing more than two O atoms for coordination. We previously reported a mixing-coordinated complex [Ni(C_5O_5)(phen)$_2$] with 1,10-phenanthroline (phen) as the first ligand and the $C_5O_5{}^{2-}$ anion as the second ligand (Chen *et al.*, 2007). The similar chelating behavior of 2,2'-bipy and 1,10-phen prompted us to replace phen ligand by 2,2'-bipy. In this report, the structure of this mixing-coordinated complex is reported.

The title compound crystalizes to the same space group as [Ni(C_5O_5)(phen)$_2$]. Both crystals have very similar cell parameters and show many common features. The chiral molecule lies across twofold axis which is along the direction of the molecular dipole moment. Around the molecular axis, two 2,2'-bipy ligands are arranged in a propeller manner. The Ni^{2+} is coordinated by four N atoms of the two 2,2'-bipy ligands and two O atoms of a croconate ligand to furnish a slightly distored octahedral NiN$_4$O$_2$ coordination core. The dihedral angle between the croconate plane and a 2,2'-bipy plane is 88.7 (1)°, and that between the two 2,2'-bipy planes is 81.9 (1)° in [Ni(C_5O_5) (2,2'-bipy)$_2$]. These are close to the corresponding dihedral angles (86.9 (1)° and 86.6 (1)°) in [Ni(C_5O_5)(phen)$_2$]. The C—O bond lengths involving coordinated O atoms are longer than those of other C—O bonds. In both crystals, molecules packed alternately along +b and-b directions.

However, we can not fail to notice some differences between the two crystals. The Ni—O band length of [Ni(C_5O_5)(2,2'-bipy)$_2$] {2.102 (2) Å} is longer than that {2.098 (3) Å} of [Ni(C_5O_5)(phen)$_2$]. Meanwhile, the Ni—N band lengths of [Ni(C_5O_5)(2,2'-bipy)$_2$] {2.059 (2), 2.066 (2) Å} is considerably shorter than those {2.071 (3), 2.088 (3) Å} of [Ni(C_5O_5)(phen)$_2$]. It seems that 2,2'-bipyridine is a stronger ligand to Ni^{2+} in comparison with 1,10-phenanthroline. The crystal structure is stabilized by intermolecular C—H⋯O hydrogen bonds (Table 1).

Experimental

[K$_2$(C_5O_5)] (0.050 g, 0.23 mmol) and NiCl$_2$.6H$_2$O (0.060 g, 0.25 mmol) were dissolved in mixed solvent of water (15 ml) and dimethylformamide (10 ml). Then 2,2'-bipy (0.080 g, 0.51 mmol) was added. The mixture was heated to 340–350 K under continuous stirring for 20 min and then filtered. The green-yellow prisms crystals were obtained by slow evaporation at 313 K.

supplementary materials

Refinement

All H atoms were positioned geometrically and allowed to ride on their attached atom. The C—H bond lengths for aromatic groups were set to 0.93 Å.
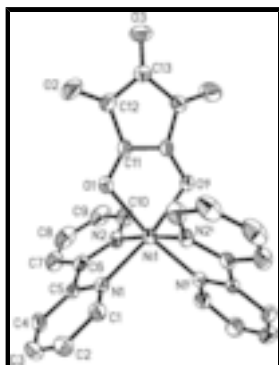
Figures

Fig. 1. The molecular structure of $[Ni(C_5O_5)(2,2'\text{-bipy})_2]$. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [symmetry code: (i) $-x + 1$, y, $-z + 3/2$.]

Bis(2,2'-bipyridine-$\kappa^2 N,N'$)(croconato-$\kappa^2 O,O'$)nickel(II)

Crystal data

$[Ni(C_5O_5)(C_{10}H_8N_2)_2]$	$F_{000} = 1048$
$M_r = 511.13$	$D_x = 1.577$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
Hall symbol: -P_2n 2ab	Cell parameters from 2518 reflections
$a = 12.725$ (5) Å	$\theta = 2.5$–$23.4°$
$b = 10.752$ (5) Å	$\mu = 0.95$ mm^{-1}
$c = 15.733$ (5) Å	$T = 293$ (2) K
$V = 2152.6$ (15) Å^3	Prism, green-yellow
$Z = 4$	$0.20 \times 0.19 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	2466 independent reflections
Radiation source: fine-focus sealed tube	1536 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.089$
Detector resolution: 10.0 pixels mm^{-1}	$\theta_{max} = 27.5°$
$T = 293(2)$ K	$\theta_{min} = 2.5°$
φ and ω scans	$h = -15 \rightarrow 16$
Absorption correction: multi-scan (APEX2; Bruker, 2005)	$k = -13 \rightarrow 10$
$T_{min} = 0.821$, $T_{max} = 0.902$	$l = -20 \rightarrow 19$

10055 measured reflections

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 0.0108P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2466 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Ni1	0.5000	0.46011 (4)	0.2500	0.03546 (17)
O1	0.56048 (15)	0.31353 (15)	0.17633 (10)	0.0439 (5)
O2	0.6016 (2)	0.0512 (2)	0.12408 (16)	0.1053 (10)
O3	0.5000	−0.1097 (3)	0.2500	0.0700 (9)
N1	0.45364 (18)	0.58822 (19)	0.34037 (12)	0.0397 (5)
N2	0.63184 (17)	0.46676 (19)	0.32573 (12)	0.0419 (6)
C1	0.3650 (3)	0.6535 (3)	0.34092 (17)	0.0531 (8)
H1	0.3173	0.6410	0.2970	0.064*
C2	0.3402 (3)	0.7384 (3)	0.4029 (2)	0.0717 (10)
H2	0.2774	0.7824	0.4013	0.086*
C3	0.4114 (4)	0.7561 (3)	0.4673 (2)	0.0742 (11)
H3	0.3977	0.8142	0.5097	0.089*
C4	0.5025 (3)	0.6888 (3)	0.46926 (18)	0.0570 (9)
H4	0.5502	0.6989	0.5135	0.068*
C5	0.5226 (2)	0.6052 (2)	0.40425 (15)	0.0406 (7)
C6	0.6200 (2)	0.5320 (2)	0.39824 (16)	0.0431 (7)
C7	0.6964 (3)	0.5264 (3)	0.4613 (2)	0.0638 (9)

H7	0.6872	0.5696	0.5119	0.077*
C8	0.7854 (3)	0.4569 (4)	0.4486 (2)	0.0770 (12)
H8	0.8367	0.4526	0.4906	0.092*
C9	0.7982 (2)	0.3940 (3)	0.3737 (2)	0.0679 (10)
H9	0.8587	0.3479	0.3633	0.081*
C10	0.7195 (2)	0.4008 (3)	0.31437 (19)	0.0575 (8)
H10	0.7276	0.3572	0.2637	0.069*
C11	0.5300 (2)	0.2129 (3)	0.21214 (15)	0.0393 (6)
C12	0.5511 (3)	0.0864 (3)	0.18605 (18)	0.0530 (8)
C13	0.5000	0.0035 (4)	0.2500	0.0487 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0404 (3)	0.0388 (3)	0.0271 (2)	0.000	−0.0053 (2)	0.000
O1	0.0587 (13)	0.0418 (11)	0.0310 (9)	−0.0040 (10)	0.0083 (9)	0.0013 (8)
O2	0.167 (3)	0.0586 (15)	0.0903 (17)	−0.0026 (15)	0.0769 (19)	−0.0177 (13)
O3	0.086 (2)	0.0405 (17)	0.084 (2)	0.000	0.0118 (18)	0.000
N1	0.0510 (14)	0.0360 (12)	0.0322 (11)	−0.0008 (12)	−0.0020 (11)	0.0015 (10)
N2	0.0437 (14)	0.0480 (14)	0.0340 (12)	0.0003 (12)	−0.0082 (10)	0.0017 (10)
C1	0.064 (2)	0.0507 (18)	0.0443 (16)	0.0138 (17)	0.0003 (16)	0.0011 (14)
C2	0.098 (3)	0.057 (2)	0.060 (2)	0.024 (2)	0.022 (2)	−0.0018 (17)
C3	0.119 (3)	0.048 (2)	0.056 (2)	−0.002 (2)	0.028 (2)	−0.0121 (16)
C4	0.084 (2)	0.0514 (17)	0.0359 (15)	−0.022 (2)	0.0095 (16)	−0.0076 (13)
C5	0.0582 (19)	0.0341 (14)	0.0295 (13)	−0.0130 (14)	0.0012 (12)	0.0026 (11)
C6	0.0535 (18)	0.0442 (16)	0.0317 (14)	−0.0198 (15)	−0.0080 (13)	0.0070 (13)
C7	0.076 (2)	0.068 (2)	0.0482 (18)	−0.023 (2)	−0.0272 (17)	0.0038 (15)
C8	0.065 (2)	0.090 (3)	0.076 (3)	−0.023 (2)	−0.041 (2)	0.033 (2)
C9	0.0442 (18)	0.080 (3)	0.079 (2)	0.0036 (19)	−0.0144 (18)	0.026 (2)
C10	0.0494 (19)	0.067 (2)	0.0555 (19)	0.0078 (18)	−0.0081 (15)	0.0055 (16)
C11	0.0431 (17)	0.0439 (16)	0.0309 (13)	−0.0025 (14)	−0.0005 (11)	−0.0019 (12)
C12	0.066 (2)	0.0462 (17)	0.0463 (17)	−0.0038 (17)	0.0129 (16)	−0.0085 (14)
C13	0.052 (2)	0.042 (2)	0.052 (2)	0.000	0.000 (2)	0.000

Geometric parameters (Å, °)

Ni1—N2	2.059 (2)	C3—C4	1.367 (4)
Ni1—N2[i]	2.059 (2)	C3—H3	0.9300
Ni1—N1	2.066 (2)	C4—C5	1.385 (4)
Ni1—N1[i]	2.066 (2)	C4—H4	0.9300
Ni1—O1[i]	2.1022 (18)	C5—C6	1.472 (4)
Ni1—O1	2.1022 (18)	C6—C7	1.389 (4)
O1—C11	1.280 (3)	C7—C8	1.371 (5)
O2—C12	1.227 (3)	C7—H7	0.9300
O3—C13	1.217 (5)	C8—C9	1.369 (5)
N1—C1	1.328 (3)	C8—H8	0.9300
N1—C5	1.347 (3)	C9—C10	1.370 (4)
N2—C10	1.334 (3)	C9—H9	0.9300

N2—C6	1.347 (3)	C10—H10	0.9300
C1—C2	1.372 (4)	C11—C11^{i}	1.415 (5)
C1—H1	0.9300	C11—C12	1.446 (4)
C2—C3	1.373 (5)	C12—C13	1.493 (4)
C2—H2	0.9300	C13—C12^{i}	1.493 (4)
N2—Ni1—N2^{i}	176.02 (12)	C3—C4—C5	118.9 (3)
N2—Ni1—N1	79.12 (9)	C3—C4—H4	120.6
N2^{i}—Ni1—N1	98.19 (8)	C5—C4—H4	120.6
N2—Ni1—N1^{i}	98.19 (8)	N1—C5—C4	121.3 (3)
N2^{i}—Ni1—N1^{i}	79.12 (9)	N1—C5—C6	115.4 (2)
N1—Ni1—N1^{i}	96.35 (11)	C4—C5—C6	123.3 (3)
N2—Ni1—O1^{i}	90.30 (8)	N2—C6—C7	120.2 (3)
N2^{i}—Ni1—O1^{i}	92.68 (8)	N2—C6—C5	115.3 (2)
N1—Ni1—O1^{i}	90.91 (8)	C7—C6—C5	124.5 (3)
N1^{i}—Ni1—O1^{i}	169.72 (7)	C8—C7—C6	119.8 (3)
N2—Ni1—O1	92.68 (8)	C8—C7—H7	120.1
N2^{i}—Ni1—O1	90.30 (8)	C6—C7—H7	120.1
N1—Ni1—O1	169.72 (7)	C9—C8—C7	119.5 (3)
N1^{i}—Ni1—O1	90.91 (8)	C9—C8—H8	120.2
O1^{i}—Ni1—O1	82.88 (10)	C7—C8—H8	120.2
C11—O1—Ni1	106.29 (15)	C8—C9—C10	118.2 (3)
C1—N1—C5	118.5 (2)	C8—C9—H9	120.9
C1—N1—Ni1	126.82 (19)	C10—C9—H9	120.9
C5—N1—Ni1	114.72 (18)	N2—C10—C9	123.2 (3)
C10—N2—C6	118.9 (2)	N2—C10—H10	118.4
C10—N2—Ni1	125.83 (19)	C9—C10—H10	118.4
C6—N2—Ni1	114.66 (19)	O1—C11—C11^{i}	122.26 (14)
N1—C1—C2	123.5 (3)	O1—C11—C12	127.9 (2)
N1—C1—H1	118.3	C11^{i}—C11—C12	109.83 (15)
C2—C1—H1	118.3	O2—C12—C11	127.8 (3)
C1—C2—C3	117.7 (3)	O2—C12—C13	125.4 (3)
C1—C2—H2	121.1	C11—C12—C13	106.8 (2)
C3—C2—H2	121.1	O3—C13—C12^{i}	126.64 (17)
C4—C3—C2	120.2 (3)	O3—C13—C12	126.64 (17)
C4—C3—H3	119.9	C12^{i}—C13—C12	106.7 (3)
C2—C3—H3	119.9		
N2—Ni1—O1—C11	90.49 (17)	C1—N1—C5—C6	−178.6 (2)
N2^{i}—Ni1—O1—C11	−92.14 (18)	Ni1—N1—C5—C6	1.2 (3)
N1—Ni1—O1—C11	53.7 (5)	C3—C4—C5—N1	−1.0 (4)
N1^{i}—Ni1—O1—C11	−171.27 (17)	C3—C4—C5—C6	177.3 (3)
O1^{i}—Ni1—O1—C11	0.52 (13)	C10—N2—C6—C7	−2.5 (4)
N2—Ni1—N1—C1	174.7 (2)	Ni1—N2—C6—C7	169.1 (2)
N2^{i}—Ni1—N1—C1	−2.3 (2)	C10—N2—C6—C5	178.1 (2)
N1^{i}—Ni1—N1—C1	77.5 (2)	Ni1—N2—C6—C5	−10.3 (3)

O1^i—Ni1—N1—C1	−95.2 (2)	N1—C5—C6—N2	6.1 (3)
O1—Ni1—N1—C1	−147.8 (4)	C4—C5—C6—N2	−172.3 (2)
N2—Ni1—N1—C5	−5.04 (17)	N1—C5—C6—C7	−173.3 (2)
N2^i—Ni1—N1—C5	177.93 (18)	C4—C5—C6—C7	8.3 (4)
N1^i—Ni1—N1—C5	−102.20 (19)	N2—C6—C7—C8	1.8 (4)
O1^i—Ni1—N1—C5	85.09 (18)	C5—C6—C7—C8	−178.8 (3)
O1—Ni1—N1—C5	32.5 (5)	C6—C7—C8—C9	0.2 (5)
N1—Ni1—N2—C10	179.3 (2)	C7—C8—C9—C10	−1.5 (5)
N1^i—Ni1—N2—C10	−85.7 (2)	C6—N2—C10—C9	1.2 (4)
O1^i—Ni1—N2—C10	88.5 (2)	Ni1—N2—C10—C9	−169.4 (2)
O1—Ni1—N2—C10	5.6 (2)	C8—C9—C10—N2	0.8 (5)
N1—Ni1—N2—C6	8.43 (17)	Ni1—O1—C11—C11^i	−1.5 (4)
N1^i—Ni1—N2—C6	103.37 (17)	Ni1—O1—C11—C12	−179.9 (2)
O1^i—Ni1—N2—C6	−82.44 (17)	O1—C11—C12—O2	−0.7 (5)
O1—Ni1—N2—C6	−165.32 (17)	C11^i—C11—C12—O2	−179.3 (3)
C5—N1—C1—C2	0.6 (4)	O1—C11—C12—C13	178.9 (2)
Ni1—N1—C1—C2	−179.1 (2)	C11^i—C11—C12—C13	0.3 (4)
N1—C1—C2—C3	0.1 (5)	O2—C12—C13—O3	−0.6 (4)
C1—C2—C3—C4	−1.2 (5)	C11—C12—C13—O3	179.89 (13)
C2—C3—C4—C5	1.7 (5)	O2—C12—C13—C12^i	179.4 (4)
C1—N1—C5—C4	−0.1 (4)	C11—C12—C13—C12^i	−0.11 (13)
Ni1—N1—C5—C4	179.63 (19)		

Symmetry codes: (i) −x+1, y, −z+1/2.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1^{ii}	0.93	2.57	3.340 (4)	141
C8—H8···O2^{iii}	0.93	2.24	3.114 (4)	156
C9—H9···O3^{iv}	0.93	2.57	3.222 (4)	127

Symmetry codes: (ii) x, −y+1, z+1/2; (iii) −x+3/2, −y+1/2, z+1/2; (iv) x+1/2, y+1/2, −z+1/2.

Fig. 1