Se2—Fe—Se3	117.76 (2)	C7—Se3—Fe	111.06 (12)
Se1—Fe—Se3	106.51 (5)	Fe^i—Se3—Fe	74.75 (1)
$Se3^i$—Fe—Se3	105.25 (3)		

Symmetry code: (i) $-x, 1-y, 1-z$.

Crystals of the title compounds were mounted on a glass capillary with silicone grease and quickly put into the cold nitrogen stream of the cooling device of the goniometer. The intensity data were corrected for Lorentz, polarization and absorption effects. After anisotropic refinement of this model, H atoms were added in idealized positions. One common isotropic displacement parameter per group was refined for the otherwise riding H atoms.

For both compounds, data collection: *P3 Software* (Siemens, 1990*a*); cell refinement: *P3 Software*; data reduction: *XDISK* (Siemens, 1990*b*); program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL93*.

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Diaquabis(2,2′-bipyridine-*N*,*N*′)nickel(II) diperchlorate

Yolanda Rodríguez-Martín, Javier González-Platas and Catalina Ruiz-Pérez

Grupo de Rayos X, Departamanto Física Fundamental II, Universidad de La Laguna, Avda. Astrofísico Fco. Sánchez s/n, E-38204 La Laguna, Tenerife, Spain. E-mail: caruiz@ull.es

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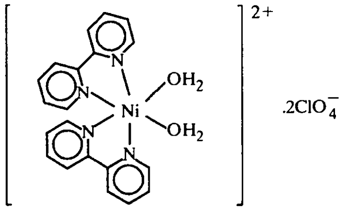
Abstract

The structure of the title compound, $[Ni(C_{10}H_8N_2)_2(H_2O)_2](ClO_4)_2$, consists of monomeric $[Ni(bipy)_2(H_2O)_2]^{2+}$ cations (bipy is 2,2′-bipyridine) and perchlorate anions. The Ni atom has octahedral coordination comprised of two water O atoms and four N atoms from two chelating bipy groups [mean values: Ni—O_{water} 2.089 (5) and Ni—N_{bipy} 2.066 (6) Å]. Hydrogen bonding plays an important role in consolidating the crystal structure.

Comment

Much work has been devoted to the study of ligand complexes because of their key role in biological processes (Sigel, 1975; Martín & Prados, 1974; Bauer & Smith, 1965) and their properties in areas such as analytical chemistry, catalysis and magneto-chemistry (De Munno *et al.*, 1993). Of these, two of the best studied groups, both in solution (Castro *et al.*, 1991) and the solid state (Kahn, 1985), are copper(II) and nickel(II) complexes with *N*-donor ligands.

In view of this interest, and as part of our research program on solid-state reactivity of first-row transition metal complexes with polydentate *N*-donor ligands (Rodríguez-Martín *et al.*, 1999; Hernández-Molina, Ruiz-Pérez, González-Platas, Sanchiz *et al.*, 1999; Hernández-Molina, Ruiz-Pérez, González-Platas & Lorenzo-Luis, 1999), we report here the preparation and crystal structure of the complex $[Ni(bipy)_2(H_2O)_2](ClO_4)_2$ (bipy is 2,2′-bipyridine), (I).



(I)

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The choice of 2,2′-bipyridine was determined first by the assumption that such a ligand is capable of giving very stable species in solution (Sigel, 1980) due to π-back-bonding from the metal to the aromatic amine. Secondly, solid-state structures of chemical species containing π-aromatic systems are stabilized by stacking interactions involving the π systems. These non-covalent interactions control many molecular recognition and self-assembly processes in solution and the solid state, and exercise important effects on the organization and properties of many materials in areas such as biology, crystal engineering and materials science (Stoddart, 1991; Hunter, 1993; Dahl, 1994).

The crystal structure of the title compound consists of monomeric $[Ni(bipy)_2(H_2O)_2]^{2+}$ cations and perchlorate anions. As illustrated in Fig. 1, the Ni atom has octahedral coordination comprised of two water O atoms and four N atoms from two chelating bipy groups. The *N*-donor ligands show a *cis* arrangement of the two donor atoms around the Ni^{II} ion. The Ni—N_{bipy} bond distances [mean value 2.066 (6) Å] are slightly shorter that the Ni—O_{water} bond lengths [mean value 2.089 (5) Å]. The N—Ni—N bite angles [79.2 (1) and 79.5 (1)°] deviate greatly from the ideal angle of 90° because of the constrained geometry of the bipyridine ring system (Merrit & Schroeder, 1956). These values 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, Ruiz-Pérez, González-Platas, Sanchiz *et al.*, 1999).

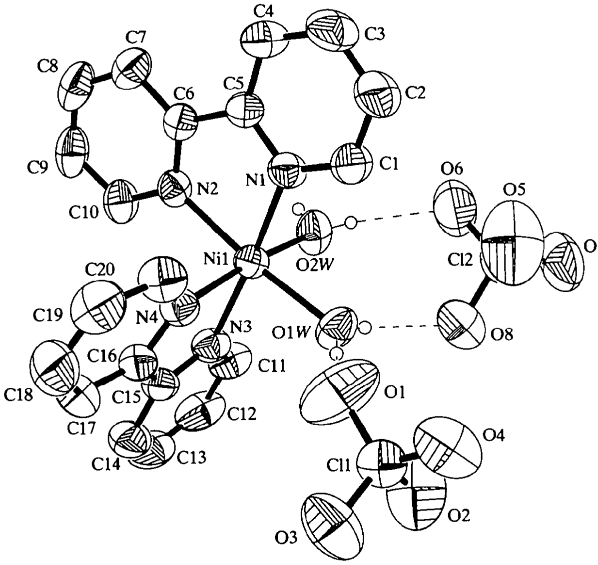

Fig. 1. The structure of the title molecule. Ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii. H atoms attached to carbon have been omitted and O—H···O-type hydrogen bonds are indicated by broken lines.

The best equatorial plane of the NiN_4O_2 chromophore is defined by atoms N1, N2, N3 and O1*W* [largest deviation from the mean plane is 0.034 (2) Å for N3], and the Ni atom is 0.001 (3) Å out of this plane.

As expected, the individual pyridine rings of the two bipy ligands are nearly planar [the largest deviation from the mean planes is 0.092 (4) Å at C18]. However, the bipy ligands as a whole are far from being planar, and the dihedral angles between the six-membered pyridyl rings in the bipy ligands are 4.2 (1) and 5.5 (1)°. Such dihedral twist motion is perfectly normal for a coordinated bipy ligand and angles up to 18° have been observed previously in bipy complexes (Cano *et al.*, 1994). The average C—C [1.375 (5) Å] and C—N [1.342 (4) Å] bond lengths within the rings, and the inter-ring C—C bonds [1.487 (4) Å] are in good agreement with those given in the literature for non-coordinated bipy (Merrit & Schroder, 1956; Wada *et al.*, 1976; Osakada & Yamamoto, 1984; Cortés *et al.*, 1994). Although the mean angle within the individual pyridine rings is the expected 120°, deviations from this angle are observed for inter-ring angles C_{ring1}—C_{ring2}—N_{ring2} [115.3 (2)°] and C_{ring1}—C_{ring2}—C_{ring2} [123.7 (3)°].

The two bipy ligands around the Ni atom are almost perpendicular to each other, the dihedral angle between the bipy mean planes being 81.77 (5)°.

The water molecules linked to the Ni^{II} atom are hydrogen bonded to the ClO_4^- anions (Table 2). There are also some weak C—H···O contacts which involve the C atoms of the bipy ligands as hydrogen donors, and perchlorate and water O atoms as acceptors. Not all the C—H···O contacts can be considered as hydrogen bonds, but they are indicative of some polarization. The importance of C—H···O and C—H···O*W* hydrogen bonds has long been known to spectroscopists and crystallographers, but definitive evidence of their structural significance was produced only a few years ago (Taylor & Kennard, 1982; Desiraju, 1991; Steiner & Saenger, 1993). In nitrogen-containing molecules, the inductive effect of neutral or charged N atoms decreases the electron density in immediately adjacent CH groups (C_α atoms) and enhances the facility with which they participate in C···H···*X* hydrogen bonds, being usually the shortest ones. However, in the present case, all of the C_α atoms are not available, due to the bipy coordination geometry, and only the C1 and C11 atoms form C—H···O contacts. The remaining contacts involve the C atoms β to N atoms (C_α to the inter-ring C atoms), whose H atoms are outer and have been determined to be the most acidic protons on the ring (Constable & Seddon, 1982).

Experimental

A mixture of $Ni(ClO_4)_2\cdot6H_2O$ (1.85 g, 2.0 mmol) and bipy (0.78 g, 2.0 mmol) was disolved in $EtOH/H_2O$ (1:1) (10 ml, 333 K, pH 2). The resulting solution was allowed to stand in air overnight and a violet precipitate was deposited. Recrystallization from water gave the title complex.

Crystal data

$[Ni(C_{10}H_8N_2)_2(H_2O)_2]$-$(ClO_4)_2$
$M_r = 606.01$
Monoclinic
$P2_1/n$
$a = 10.003\ (1)$ Å
$b = 14.744\ (1)$ Å
$c = 17.242\ (2)$ Å
$\beta = 92.14\ (1)°$
$V = 2541.1\ (4)$ Å^3
$Z = 4$
$D_x = 1.584$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.97–20.28°$
$\mu = 1.034$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.57 × 0.44 × 0.30 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.527$, $T_{\max} = 0.733$
7590 measured reflections
7374 independent reflections

4959 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 29.97°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.143$
$S = 1.012$
7374 reflections
347 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 1.1522P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.621$ e Å^{-3}
$\Delta\rho_{\min} = -0.460$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—N4	2.061 (2)	Ni1—N2	2.075 (2)
Ni1—N3	2.062 (2)	Ni1—O1*W*	2.084 (2)
Ni1—N1	2.066 (2)	Ni1—O2*W*	2.094 (2)
N4—Ni1—N3	79.49 (10)	O1*W*—Ni1—O2*W*	87.84 (9)
N1—Ni1—N2	79.20 (9)		

Table 2. *Hydrogen-bonding and short-contact geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O8	0.65 (5)	2.21 (5)	2.852 (5)	178 (6)
O1*W*—H12*W*···O1	0.73 (5)	2.19 (5)	2.874 (5)	157 (4)
O2*W*—H21*W*···O4$^{\rm i}$	0.75 (5)	2.09 (5)	2.839 (4)	179 (5)
O2*W*—H22*W*···O6	0.76 (5)	2.04 (5)	2.795 (5)	172 (5)
C9—H9···O2$^{\rm ii}$	0.93	2.47	3.276 (5)	145
C11—H11···O2*W*	0.93	2.54	3.089 (4)	119
C12—H12···O5$^{\rm iii}$	0.93	2.51	3.386 (6)	157

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

The perchlorate ions had large displacement parameters, indicating that some disorder is present, but attempts to introduce a disorder model for the O atoms were unsuccessful. H atoms bonded to C atoms were constrained and the coordinates for those of the water molecules were refined freely and with equal $U_{\rm iso}$(H) parameters.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1997). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEX* (McArdle, 1993). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1527). Services for accessing these data are described at the back of the journal.

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Chloro(pentamethyl-η^5-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II)

ILIA A. GUZEI,[a] M. ANGELES PAZ-SANDOVAL,[b] ROMÁN TORRES-LUBIÁN[b] AND PATRICIA JUÁREZ-SAAVEDRA[b]

[a]*Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011, USA, and* [b]*Centro de Investigación y Estudios Avanzados del IPN, Departamento de Química, Apartado Postal 14-740, 07000 México DF, México. E-mail: iguzei@iastate.edu*

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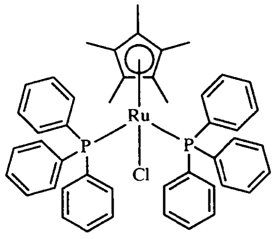
Abstract

The crystal structure of the title compound, $[RuCl(C_{10}H_{15})(C_{18}H_{15}P)_2]$, is reported. A structural discussion and a comparison with similar ruthenium(II) complexes are presented.

Comment

The crystal structure of the title compound, (1), completes our structural characterization of the series of pentamethylcyclopentadienyl- and cyclopentadienylruthenium(II) bis(triphenylphosphine) complexes (Torres-Lubián & Paz-Sandoval, 1997).



(1)

The easily prepared $Cp^*RuCl(PPh_3)_2$ (Chinn & Heinekey, 1990) is an important precursor to other half-sandwich complexes of ruthenium(II). It has been widely used due to the lability of the ligands (Yi *et al.*, 1997, 1998; Sato & Kawata, 1997; Bruce *et al.*, 1996; Davies *et al.*, 1990, and references therein). Despite its wide use as a starting material in many syntheses by many research groups, compound (1) has not been structurally characterized. There are several analogous compounds, however, and we deemed it imperative to compare them to (1).

The molecular structure of the neutral complex (1) is shown in Fig. 1. The relevant bond distances and angles are listed in Table 1. The molecule can be considered as a member of the $M(C_5R_5)(PR'_3)_2Cl$ series, and the geometry around the Ru atom can be described as distorted octahedral if the Cp* group is viewed as a tridentate ligand. The ruthenium–carbon distances range between 2.224 (2) and 2.274 (2) Å [average 2.24 (2) Å]. These bond lengths are in good agreement with the corresponding distances in related compounds: $CpRu(PPh_3)_2Cl$ [(2); Bruce *et al.*, 1981], $Cp^*Ru[P(p\text{-}CF_3C_6H_4)_3]_2Cl$ [(3); Serron *et al.*, 1995], $CpRu[P(p\text{-}CF_3C_6H_4)_3]_2Cl$ [(4); Serron *et al.*, 1995], $Cp^*Ru(PPh_3)(PPh_2H)Cl$ [(5); Torres-Lubián & Paz-Sandoval, 1997], $CpRu(PPh_3)(PPh_2H)Cl$ [(6); Torres-Lubián & Paz-Sandoval, 1997], $Cp^*Ru(PPh_2H)_2Cl$ [(7); Torres-Lubián & Paz-Sandoval, 1997] and $CpRu(\eta^1\text{-dppm})_2Cl$ [(8); Orth *et al.*, 1996]. The Ru—C bond lengths in (1) are slightly longer than the Ru—C distances [2.192 (3)–2.220 (3) Å] in (2) due to the steric strain introduced by the Cp* moiety. The bulkiness of the Cp* ligand also results in a wider variation of the ruthenium–carbon distances in (1). The Ru–centroid distance [1.887 (2) Å] is somewhat longer than that in (2) [1.847 (4) Å], but is

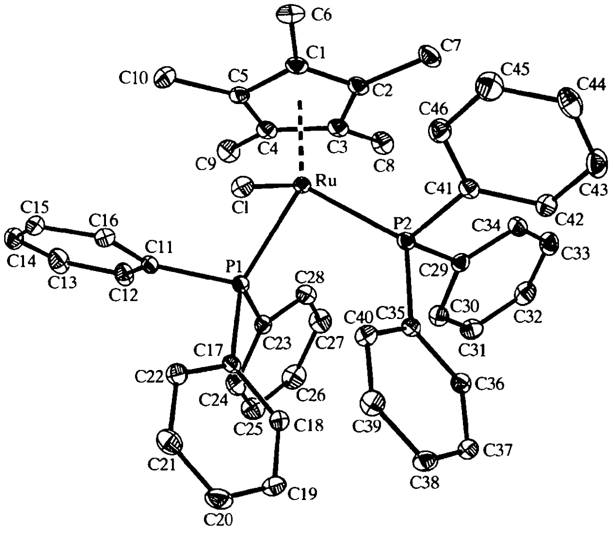


Fig. 1. The molecular structure of (1). The displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.