Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

[Bis[tris(3,5-dimethylpyrazolyl)methane]nickel(II)][tetrachloronickelate(II)]–methanol–water (1/1/1)

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Received 1 April 2005
Accepted 11 April 2005
Online 16 April 2005

Key indicators

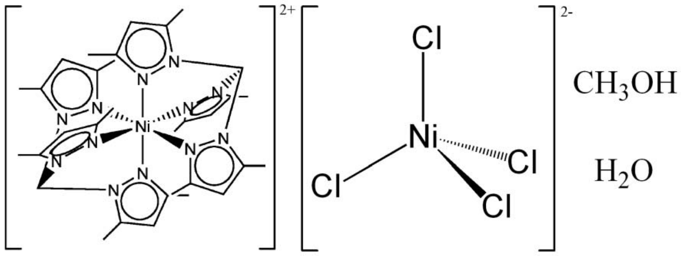
Single-crystal X-ray study
T = 220 K
Mean σ(C–C) = 0.003 Å
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.156
Data-to-parameter ratio = 17.0

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

The title complex, $[Ni(HC(3,5\text{-}Me_2pz)_3)_2][NiCl_4]\cdot CH_3OH\cdot H_2O$, where $HC(3,5\text{-}Me_2pz)_3$ is tris(3,5-dimethylpyrazolyl)methane ($C_{16}H_{22}N_6$), contains two octahedral nickel(II) cationic complexes, each having $\overline{1}$ symmetry. The Ni atom in each cation is coordinated by six pyrazolyl rings of two chelating $HC(3,5\text{-}Me_2pz)_3$ ligands, with Ni—N distances between 2.0870 (16) Å and 2.1094 (16) Å. The anion consists of nickel(II) surrounded tetrahedrally by four Cl^- anions, with Ni—Cl distances between 2.2547 (7) Å and 2.2847 (7) Å. There is also one methanol molecule and one disordered water molecule in the asymmetric unit.

Comment

The discovery of polypyrazolylmethane ligands by Trofimenko (1970) had a major impact in the field of inorganic and organometallic chemistry. In our constant search for new and efficient complexes that could catalyze a large range of chemical reactions, we became interested in the synthesis of nickel(II) polypyrazolyl complexes. In the course of our studies, the synthesis of $[\{HC(3,5\text{-}Me_2pz)_3\}_2Ni][NiCl_4]$ was performed [$HC(3,5\text{-}Me_2pz)_3$ is tris(3,5-dimethylpyrazolyl)methane]. The compound obtained here is similar to those previously reported by our group (Michaud *et al.*, 2005) and by Reger *et al.* (2002), using, respectively, $NiBr_2$ and $Ni(BF_4)_2\cdot 3H_2O$ as precursors. The main difference between the crystal structures of $[Ni(HC(3,5\text{-}Me_2pz)_3)_2]Br_2$ (I-Br), $[Ni(HC(3,5\text{-}Me_2\ pz)_3)_2](BF_4)_2$ (I-BF_4) and the title compound, (I-$NiCl_4$), is the different counterion. All three complexes crystallize in the monoclinic system, but (I-Br) and (I-BF_4) have *C*-centered unit cells, compared with a primitive cell for (I-$NiCl_4$), which is obtained as a mixed solvate of methanol and water.



(I-$NiCl_4$)

The two crystallographically independent cations in the title compound are located on inversion centers (Figs. 1 and 2), resulting in only three unique Ni—N bond distances for each

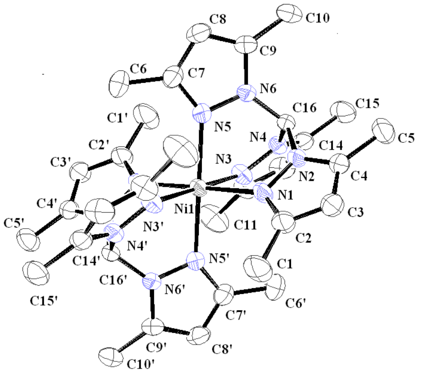


Figure 1

A drawing of the first independent cation of (I-NiCl$_4$), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. Primed atoms (′) are related by the symmetry operator ($2 - x$, $1 - y$, $1 - z$).

(Table 1). In both cases, the Ni^{II} cations adopt a pseudo-octahedral geometry. The *cis* N—Ni—N angles within each tridentate ligand of (I-NiCl$_4$) are equivalent [85.26 (6)–86.28 (6)°] and are comparable with those found in (I-Br) [85.65 (11) and 86.53 (7)°] and (I-BF$_4$) [85.30 (9)–86.26 (9)°]; the average value of these angles in one compound is within the experimental error of the others [85.8 (3)° for (I-NiCl$_4$), compared with 86.2 (3)° for (I—Br) and 85.9 (3)° for (I-BF$_4$)]. The range of Ni—N distances varies only slightly in (I-NiCl$_4$) [2.087 (2)–2.109 (2) Å] compared with (I—Br) [2.0754 (17)–2.110 (3) Å] and (I—BF$_4$) [2.076 (2)–2.096 (2) Å].

The anion contains Ni^{II} coordinated tetrahedrally by four Cl$^-$ anions. The average of the Cl—Ni—Cl angles is 109°, as expected, but one of the angles, Cl1—Ni3—Cl2, is significantly larger than the others [117.43 (3)°]. The Ni3—Cl distances vary from 2.2547 (4) to 2.2847 (7) Å.

The methanolic H atom is hydrogen bonded to atom Cl2, as verified by the O97⋯Cl2 and H97*D*⋯Cl2 distances of 3.332 (3) and 2.505 Å, respectively (Fig. 3). There is also a disordered water molecule in the asymmetric unit; this molecule was removed from the model using the SQUEEZE option in *PLATON* (Spek, 2003), thus leaving solvent voids of 56 Å^3. Finally, there are no chemically significant contacts between the cations and anions (Fig. 4).

Experimental

A solution of HC(3,5-Me$_2$pz)$_3$ (440 mg, 1.50 mmol) in boiling butanol was added to a suspension of NiCl$_2$·6H$_2$O (330 mg, 1.40 mmol) in boiling butanol. The reaction was stirred until all the solid suspension had dissolved and a deep-blue solid precipitated. The solution was cooled to room temperature and the resulting solid filtered. Subsequent washings with cold butanol and cold diethyl ether afforded the analytically pure compound [(HC(3,5-Me$_2$pz)$_3$)$_2$Ni][NiCl$_4$] (461 mg, 76% yield). Diffusion of diethyl ether into a solution of [(HC(3,5-Me$_2$pz)$_3$)$_2$Ni][NiCl$_4$] in methanol afforded X-ray quality crystals. Analysis, calculated for C$_{32}$H$_{44}$N$_{12}$Cl$_4$Ni$_2$: C 44.90, H 5.18, N 19.64; found: C 44.47, H 5.26, N 19.47. Spectroscopic analysis: ^{1}H NMR (CD$_3$CN, δ, p.p.m.): 3.2, −3.0, −10.0; IR (KOH, ν, cm^{-1}): 3395 (*w*), 3130–2922 (*m*), 1653 (w), 1567 (*s*), 1462–1368 (*s*), 1307 (*s*), 1258 (*s*), 1164 (*m*), 1113 (*m*), 1044 (*s*), 987 (*m*), 910 (*m*), 862 (*s*), 831 (*m*), 706 (*s*), 631 (*m*), 490 (*m*); UV–vis (CH$_3$CN, λ (nm), ε [(mol dm^{-3})$^{-1}$ cm^{-1}]: (575, 102), (618, 152), (658, 135), (701, 127), (892, 55); *Pf* > 593 K; $\mu_{\rm eff}$ 4.24.

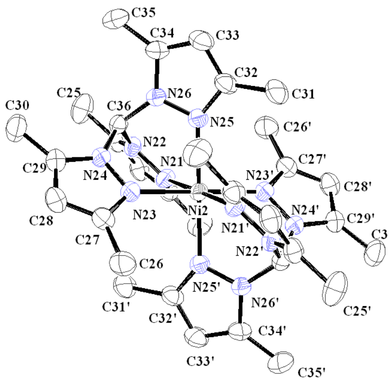


Figure 2

A drawing of the second independent cation of (I-NiCl$_4$), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. Primed atoms (′) are related by the symmetry operator ($2 - x$, $1 - y$, $-z$).

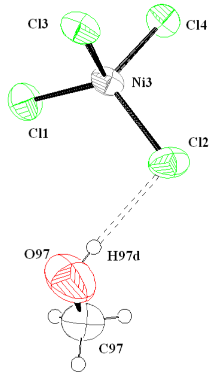


Figure 3

A drawing of the anion and the methanol of (I-NiCl$_4$), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The hydrogen bond is shown dashed.

Crystal data

[Ni(C$_{16}$H$_{22}$N$_6$)$_2$][NiCl$_4$]·CH$_4$O·H$_2$O
M_r = 906.07
Monoclinic, $P2_1/c$
a = 10.2998 (2) Å
b = 18.5245 (3) Å
c = 21.9660 (3) Å
β94.118 (1)°
V = 4180.26 (12) Å^3
Z = 4
D_x = 1.447 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 36 297 reflections
θ = 2.4–72.6°
μ = 3.85 mm^{-1}
T = 220 (2) K
Plate, blue
0.30 × 0.30 × 0.08 mm

Data collection

Bruker SMART 2K/Platform CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min}$ = 0.287, $T_{\rm max}$ = 0.740
49 482 measured reflections
8242 independent reflections
7048 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.091
$\theta_{\rm max}$ = 72.6°
h = −12 → 12
k = −22 → 21
l = −27 → 26

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.156$
$S = 1.13$
8242 reflections
485 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1017P)^2 + 0.294P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.05$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N3	2.0870 (16)	N21—N22	1.370 (2)
Ni1—N1	2.1004 (15)	N22—C24	1.361 (2)
Ni1—N5	2.1094 (16)	N23—C27	1.341 (3)
N1—C2	1.327 (2)	N23—N24	1.359 (2)
N1—N2	1.369 (2)	N24—C29	1.360 (2)
N3—C12	1.328 (2)	N25—C32	1.332 (2)
N3—N4	1.367 (2)	N25—N26	1.365 (2)
N4—C14	1.355 (2)	N26—C34	1.361 (2)
N5—C7	1.332 (2)	C22—C23	1.395 (3)
N5—N6	1.370 (2)	C23—C24	1.368 (3)
N6—C9	1.359 (2)	C27—C28	1.396 (3)
C2—C3	1.400 (3)	C28—C29	1.359 (3)
C3—C4	1.362 (3)	C32—C33	1.394 (3)
C12—C13	1.390 (3)	C33—C34	1.353 (3)
C13—C14	1.368 (3)	Ni3—Cl4	2.2547 (7)
Ni2—N21	2.0929 (16)	Ni3—Cl1	2.2568 (7)
Ni2—N23	2.1010 (15)	Ni3—Cl3	2.2649 (7)
Ni2—N25	2.1076 (15)	Ni3—Cl2	2.2847 (7)
N21—C22	1.326 (2)		
N3—Ni1—N3^{i}	180	N23^{ii}—Ni2—N23	180
N3—Ni1—N1^{i}	85.76 (6)	N21—Ni2—N25	94.74 (6)
N3—Ni1—N1	94.24 (6)	N21^{ii}—Ni2—N25	85.26 (6)
N1^{i}—Ni1—N1	180	N23^{ii}—Ni2—N25	86.28 (6)
N3—Ni1—N5^{i}	94.40 (6)	N23—Ni2—N25	93.72 (6)
N3—Ni1—N5	85.59 (6)	N25—Ni2—N25^{ii}	180
N1^{i}—Ni1—N5	86.27 (6)	Cl4—Ni3—Cl1	107.78 (3)
N1—Ni1—N5	93.73 (6)	Cl4—Ni3—Cl3	108.01 (2)
N5^{i}—Ni1—N5	180	Cl1—Ni3—Cl3	109.46 (3)
N21—Ni2—N21^{ii}	180	Cl4—Ni3—Cl2	106.58 (3)
N21—Ni2—N23^{ii}	94.60 (6)	Cl1—Ni3—Cl2	117.42 (3)
N21—Ni2—N23	85.39 (6)	Cl3—Ni3—Cl2	107.24 (3)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z$.

H atoms were constrained using a riding-model approximation, with C—H = 0.93–0.98 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}$(parent) for all others. The maximum electron-density peak of 1.05 e Å^{-3} was located 0.89 Å from atom Cl2

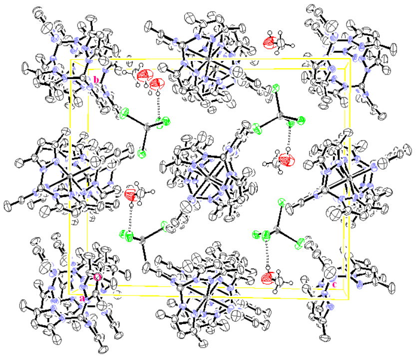

Figure 4
A drawing of the unit-cell contents of (I-$NiCl_4$). Ellipsoids are drawn at the 50% probability level and dashed lines indicate hydrogen bonds. H atoms have been omitted from the cation.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *UdMX* (local program).

Financial support from the Natural Sciences and Engineering Research Council of Canada and from the Fonds FQRNT du Ministère de l'Éducation du Québec is gratefully acknowledged.

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