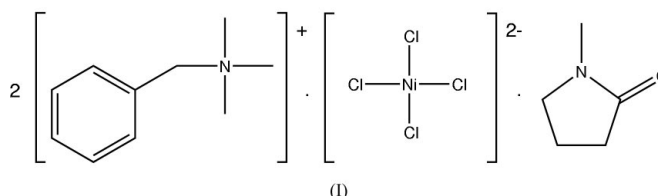


Bis(benzyltrimethylammonium) tetrachloro-
nickelate(II) *N*-methylpyrrolidin-2-one solvateHuub Kooijman,^{a*} Menno A.
Keegstra,^b Lambert Brandsma^b
and Anthony L. Spek^a^aBijvoet Center for Biomolecular Research,
Department of Crystal and Structural Chemistry,
Utrecht University, Padualaan 8, 3584 CH
Utrecht, The Netherlands, and ^bDepartment of
Preparative Organic Chemistry, Utrecht
University, Padualaan 8, 3584 CH Utrecht,
The NetherlandsCorrespondence e-mail:
h.kooijman@chem.uu.nl

Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.069
wR factor = 0.182
Data-to-parameter ratio = 15.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The title compound, $(\text{C}_{10}\text{H}_{16}\text{N})_2[\text{NiCl}_4] \cdot \text{C}_5\text{H}_9\text{NO}$, was
obtained as a side-product in a reaction of $\text{PhNiCl}(\text{PPh}_3)_2$
with quaternary ammonium ions in *N*-methylpyrrolidin-2-one.
 $\text{C}-\text{H} \cdots \text{Cl}$ interactions link the ions into two-dimensional
networks parallel to the *bc* plane.Received 15 September 2004
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Comment

Oxidative addition complexes of nickel [e.g. $\text{PhNiCl}(\text{PPh}_3)_2$]
are useful species as catalysts in nucleophilic aromatic
substitution reactions (Cassar *et al.*, 1979). In organic syn-
thesis, they are even preferable to zero-valence nickel
complexes, because of their higher stability and lower oxida-
tion sensitivity. When, however, this catalyst was applied in *N*-
methylpyrrolidin-2-one (NMP), together with a quaternary
ammonium salt, an unexpected side reaction occurred, leading
to the formation of the title compound, $(\text{BzMe}_3\text{N})_2$ -
 $[\text{NiCl}_4] \cdot \text{NMP}$ (Bz is benzyl), (I).The crystal structure determination of (I) revealed an
asymmetric unit containing one $[\text{NiCl}_4]^{2-}$ ion, two trimethyl-
benzylammonium counter-ions and an *N*-methylpyrrolidin-2-
one solvent molecule. The conformations of the ammonium
ions are virtually identical, as indicated by the torsion angles
listed in Table 1. The geometry of the tetrachloronickelate ion
deviates somewhat from a perfect tetrahedron, with bond
angles in the range $102.44(9)$ – $117.41(10)^\circ$. The NMP solvent
molecule displays a flip-flop disorder of the C22–C23 ethyl-
ene moiety (see Fig. 1). As a consequence of this disorder, the
keto moiety is also disordered over two positions.The crystal structure displays a number of short $\text{C}-\text{H} \cdots \text{A}$
contacts, all with $\text{H} \cdots \text{A}$ distances 0.14 – 0.21 \AA smaller than the
sum of their van der Waals radii; geometric details are listed in
Table 2. A number of $\text{C}-\text{H} \cdots \text{Cl}$ interactions link the ions into
an infinite two-dimensional network running parallel to the *bc*
plane (see Fig. 2). The *b* and *c* axes are also the main axes of
the plate-shaped crystal. The solvent molecules link the two-
dimensional networks into a three-dimensional network
through $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{Cl}$ interactions.

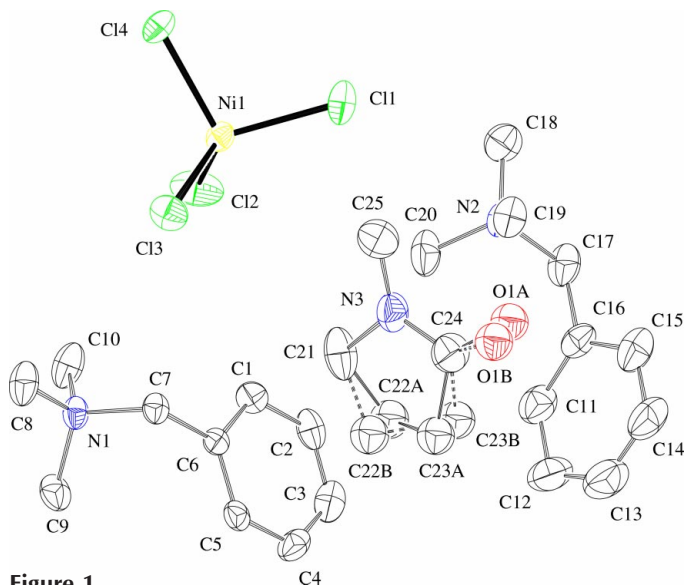


Figure 1
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms have been omitted for clarity. Both disorder components are shown.

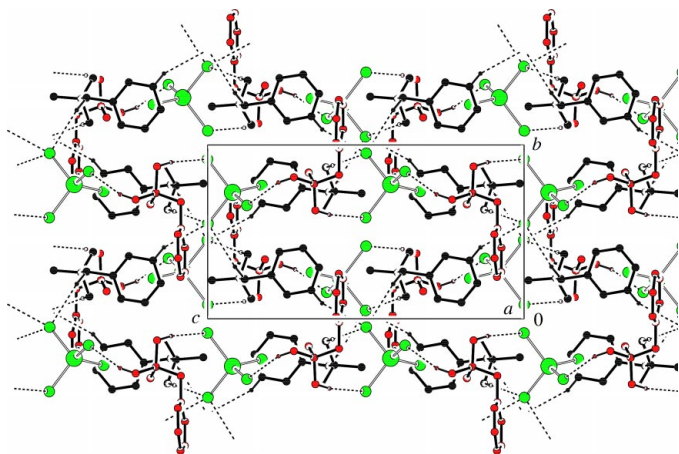


Figure 2
Projection of the crystal packing down *a*. C—H...Cl interactions link the $[NiCl_4]^{2-}$ ions (green) and benzyltrimethylammonium ions (black: the ion containing N1; red: the ion containing N2) into a two-dimensional network, parallel to the *bc* plane. H atoms not involved in the C—H...Cl interactions and the NMP solvent molecule have been omitted for clarity.

Experimental

In a 100 ml Schlenk tube, benzyltrimethylammonium chloride (2.5 mmol) was dissolved in *N*-methylpyrrolidin-2-one (NMP, 20 ml) with heating (<343 K). Subsequent addition of chlorobis(triphenylphosphine)phenylnickel(II) (2.5 mmol) to the warm (*ca* 313 K) solution resulted in the immediate formation of a blue solution. The mixture was allowed to cool down further. When diethyl ether (40 ml) was added, blue crystals precipitated together with a white powder. The solvent was decanted and the white powder was washed away with three 20 ml portions of benzene. The remaining blue solid was recrystallized by vapour diffusion using NMP as solvent and diethyl ether as precipitant.

Crystal data

$(C_{10}H_{16}N)_2[NiCl_4] \cdot C_5H_9NO$
 $M_r = 600.10$
 Monoclinic, $P2_1/c$
 $a = 18.5787$ (10) Å
 $b = 9.4933$ (15) Å
 $c = 17.3172$ (15) Å
 $\beta = 93.112$ (6)°
 $V = 3049.8$ (6) Å³
 $Z = 4$

$D_x = 1.307$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 5.9$ – 12.7°
 $\mu = 1.01$ mm⁻¹
 $T = 298$ K
 Plate, blue
 $1.25 \times 0.27 \times 0.05$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{min} = 0.753$, $T_{max} = 0.951$
 4986 measured reflections
 4812 independent reflections
 2302 reflections with $I > 2\sigma(I)$

$R_{int} = 0.052$
 $\theta_{max} = 24.2^\circ$
 $h = -21 \rightarrow 0$
 $k = -10 \rightarrow 0$
 $l = -19 \rightarrow 20$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.182$
 $S = 0.99$
 4812 reflections
 309 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0815P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.69$ e Å⁻³
 $\Delta\rho_{min} = -0.36$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—Cl1	2.258 (3)	Ni1—Cl3	2.269 (2)
Ni1—Cl2	2.231 (3)	Ni1—Cl4	2.256 (2)
Cl1—Ni1—Cl2	113.24 (9)	Cl2—Ni1—Cl3	107.43 (10)
Cl1—Ni1—Cl3	117.41 (10)	Cl2—Ni1—Cl4	111.62 (10)
Cl1—Ni1—Cl4	102.44 (9)	Cl3—Ni1—Cl4	104.27 (8)
C8—N1—C7—C6	175.3 (6)	C18—N2—C17—C16	168.6 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2...Cl4 ⁱ	0.93	2.74	3.619 (9)	158
C7—H7B...Cl4 ⁱⁱ	0.97	2.79	3.694 (8)	156
C9—H9A...Cl4 ⁱⁱⁱ	0.96	2.76	3.670 (8)	158
C17—H17B...O1B ^{iv}	0.96	2.38	3.215 (16)	144
C18—H18A...Cl3 ⁱ	0.96	2.80	3.738 (9)	165
C18—H18B...O1A ^{iv}	0.96	2.58	3.445 (15)	150
C19—H19A...O1A ^{iv}	0.96	2.53	3.403 (16)	151
C19—H19A...O1B ^{iv}	0.96	2.55	3.364 (17)	143
C19—H19C...Cl1	0.96	2.74	3.645 (8)	158
C25—H25C...Cl1	0.96	2.77	3.686 (10)	159

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

The title compound is very hygroscopic. The selected crystal was therefore sealed in a Lindemann glass capillary. Crystals of the title compound diffracted weakly. At $\sin\theta/\lambda = 0.58$ only 14% of the reflections had $I > 2\sigma(I)$. Data collection was therefore limited to reflections with $\sin\theta/\lambda < 0.58$. To accommodate a crystal of large dimensions, the diffraction experiments were carried out with β -filtered Mo $K\alpha$ radiation, a wide collimator (2 mm) and large apertures on the point detector (6.0 × 3.8 mm). The pyrrolidinone solvent molecule displayed conformational disorder in the ethylene bridge

and the keto moiety, which could be satisfactorily described with a two-site disorder model. Mild restraints were applied to enforce the same geometry on both disorder components. The occupancy of the major component refined to a value of 0.52 (2). Disordered atoms were refined with isotropic displacement parameters. Methyl moieties were refined as a rigid group, allowing for rotation around the C—C bond. Isotropic displacement parameters of H atoms were set at 1.5 or 1.2 times the equivalent isotropic displacement parameter of the carrier atom for methyl and other H atoms, respectively. The C—H distances were fixed at 0.93, 0.97 or 0.96 Å for aromatic, methylene and methyl H atoms, respectively.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON*

(Spek, 2003); software used to prepare material for publication: *PLATON*.

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