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**Key indicators**

Single-crystal X-ray study
*T* = 298 K
Mean σ(C–C) = 0.014 Å
Disorder in solvent or counterion
*R* factor = 0.069
*wR* factor = 0.182
Data-to-parameter ratio = 15.6

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



The title compound, $(C_{10}H_{16}N)_2[NiCl_4]\cdot C_5H_9NO$, was obtained as a side-product in a reaction of $PhNiCl(PPh_3)_2$ with quaternary ammonium ions in *N*-methylpyrrolidin-2-one. C—H···Cl interactions link the ions into two-dimensional networks parallel to the *bc* plane.

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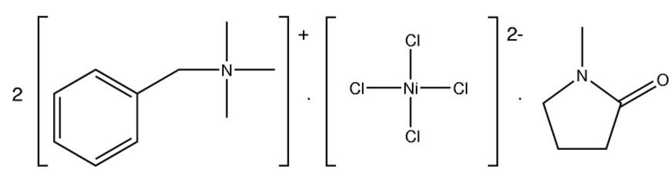
## Comment

Oxidative addition complexes of nickel [*e.g.* $PhNiCl(PPh_3)_2$] are useful species as catalysts in nucleophilic aromatic substitution reactions (Cassar *et al.*, 1979). In organic synthesis, they are even preferable to zero-valence nickel complexes, because of their higher stability and lower oxidation 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, $(BzMe_3N)_2[NiCl_4]\cdot$NMP (Bz is benzyl), (I).




(I)

The crystal structure determination of (I) revealed an asymmetric unit containing one $[NiCl_4]^{2-}$ ion, two trimethylbenzylammonium 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)°. The NMP solvent molecule displays a flip-flop disorder of the C22—C23 ethylene 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 C—H···*A* contacts, all with H···*A* distances 0.14–0.21 Å smaller than the sum of their van der Waals radii; geometric details are listed in Table 2. A number of C—H···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 C—H···O and C—H···Cl interactions.

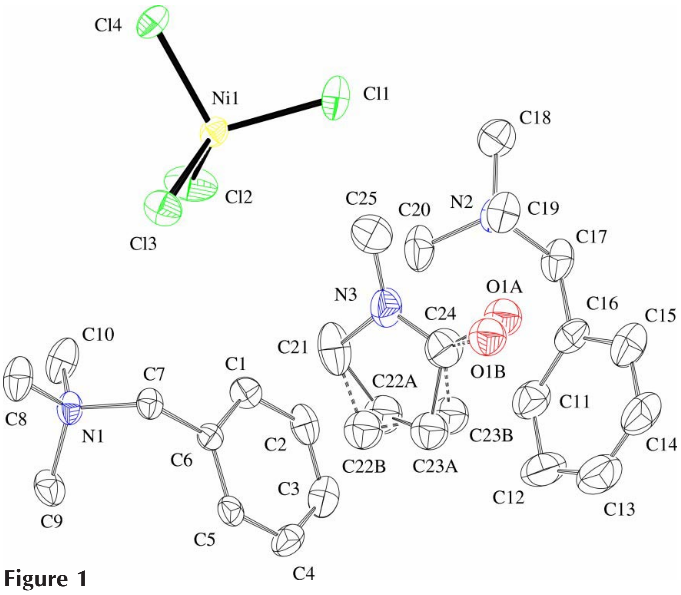



**Figure 1**
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms have been omitted for clarity. Both disorder components are shown.

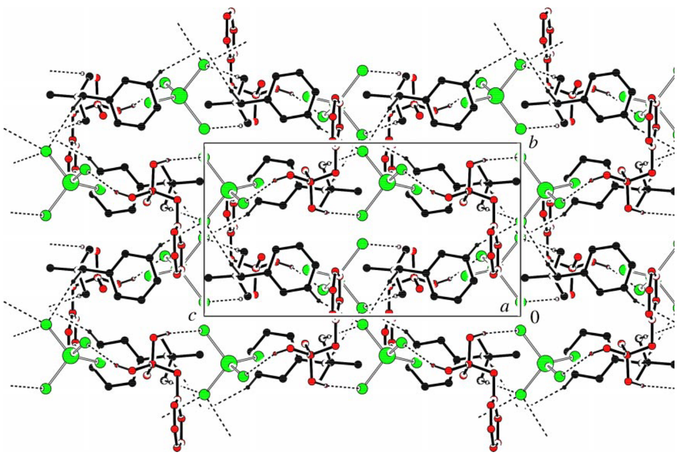



**Figure 2**
Projection of the crystal packing down $a$. C—H···Cl interactions link the $[NiCl_4]^{2-}$ ions (green) and benzyltrimethylammonium ions (black: the ion containing N1; red: the ion containing N2) into a two-dimensional network, parallel to the $bc$ plane. H atoms not involved in the C—H···Cl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

| | |
|---|---|
| $(C_{10}H_{16}N)_2[NiCl_4]\cdot C_5H_9NO$ | $D_x = 1.307$ Mg m$^{-3}$ |
| $M_r = 600.10$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 25 reflections |
| $a = 18.5787$ (10) Å | $\theta = 5.9$–$12.7°$ |
| $b = 9.4933$ (15) Å | $\mu = 1.01$ mm$^{-1}$ |
| $c = 17.3172$ (15) Å | $T = 298$ K |
| $\beta = 93.112$ (6)° | Plate, blue |
| $V = 3049.8$ (6) Å$^3$ | 1.25 × 0.27 × 0.05 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.052$ |
| $\omega/2\theta$ scans | $\theta_{max} = 24.2°$ |
| Absorption correction: analytical (de Meulenaer & Tompa, 1965) | $h = -21 \rightarrow 0$ |
| $T_{min} = 0.753$, $T_{max} = 0.951$ | $k = -10 \rightarrow 0$ |
| 4986 measured reflections | $l = -19 \rightarrow 20$ |
| 4812 independent reflections | 3 standard reflections frequency: 60 min intensity decay: 2.3% |
| 2302 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.069$ | $w = 1/[\sigma^2(F_o^2) + (0.0815P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.182$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 0.99$ | $\Delta\rho_{max} = 0.69$ e Å$^{-3}$ |
| 4812 reflections | $\Delta\rho_{min} = -0.36$ e Å$^{-3}$ |
| 309 parameters | |

**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, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2···Cl4$^{i}$ | 0.93 | 2.74 | 3.619 (9) | 158 |
| C7—H7$B$···Cl4$^{ii}$ | 0.97 | 2.79 | 3.694 (8) | 156 |
| C9—H9$A$···Cl4$^{iii}$ | 0.96 | 2.76 | 3.670 (8) | 158 |
| C17—H17$B$···O1$B^{iv}$ | 0.96 | 2.38 | 3.215 (16) | 144 |
| C18—H18$A$···Cl3$^{i}$ | 0.96 | 2.80 | 3.738 (9) | 165 |
| C18—H18$B$···O1$A^{iv}$ | 0.96 | 2.58 | 3.445 (15) | 150 |
| C19—H19$A$···O1$A^{iv}$ | 0.96 | 2.53 | 3.403 (16) | 151 |
| C19—H19$A$···O1$B^{iv}$ | 0.96 | 2.55 | 3.364 (17) | 143 |
| C19—H19$C$···Cl1 | 0.96 | 2.74 | 3.645 (8) | 158 |
| C25—H25$C$···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 $\beta$-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: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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## References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Cassar, L., Foà, M., Montanari, F. & Marinelli, G. P. (1979). *J. Organomet. Chem.* **173**, 335–339.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Sheldrick, G. M. (1986). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.