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(tert-BUTYL ISOCYANIDE) (ETHANOL) NICKEL(II) CHLORIDE

BY

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The synthesis, isolation and characterization of the stable complex \([\text{NiCl}_2(t\text{-C}_4\text{H}_9\text{NC})(\text{C}_7\text{H}_5\text{OH})]\) is described. Spectral and magnetic data are provided.

**Introduction**

The first complex containing a \([\text{Ni(CNR)}_4]^2\) cation was reported in our previous paper\(^1\). Until most recently\(^1,2\), Otsuka\(^3\) has described the only successful isolation of an isocyanide complex of divalent nickel halide \(\text{NiI}_2(t\text{-C}_4\text{H}_9\text{NC})_2\). After the submission of this paper two novel series of \(\text{Ni}^{II}\) isocyanide complexes were described\(^4,5\), one of which is \(\text{NiX}_2(t\text{-C}_4\text{H}_9\text{NC})_2\) with \(X = \text{Br}^{\Theta}, \text{NO}_3^{\Theta}, \frac{1}{2} \text{SO}_4^{2\Theta}\), and \(\frac{1}{2} \text{CO}_3^{2\Theta}\). Otsuka\(^4\) assigned a square planar coordination to this complexes with trans monovalent anions [one strong \(v(\text{NC})\) 2253 cm\(^{-1}\); \(\delta\) 1.75 ppm] and cis bidentate divalent anions [two strong \(v(\text{NC})\) 2240–2210 and 2230–2150 cm\(^{-1}\); \(\delta\) 1.00–1.35 ppm]. No spectroscopic data for the bromide complex were given. With the exception of the sulfate complex all complexes were diamagnetic. For \(X = \text{Cl}^{\Theta}\) they obtained only “an intractable brown material containing halogens”.

We wish now to report an example of a stable isocyanide complex of divalent nickel chloride, \([\text{NiCl}_2(t\text{-C}_4\text{H}_9\text{NC})(\text{C}_7\text{H}_5\text{OH})]\), which proved to be an excellent catalyst in the homogeneous polymerisation of isocyanides\(^6\).

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Results

Upon addition of one equivalent of tert-butyl isocyanide to anhydrous nickel dichloride in ethanol a transient red colour appeared. Addition of pentane to the resulting dark green, homogeneous reaction mixture led to the separation of a green solid, compound 1. A complete element analysis of 1 fitted the formula \([\text{NiCl}_2(\text{-C}_4\text{H}_9\text{NC})(\text{C}_2\text{H}_5\text{OH})]\). Measurement of the molecular weight in boiling ethanol showed the complex to be monomeric under these conditions. Conductivity data in ethanol indicate a non ionic structure\(^2\) (see experimental part). Repeated attempts to prepare the compounds \(\text{NiCl}_2(\text{-C}_4\text{H}_9\text{NC})_n\) with \(n = 2-4\) have so failed. Mixing the corresponding stoichiometric amounts of isocyanide either with nickel dichloride or with 1 with or without an appropriate solvent at low temperatures always yielded dark green to dark red-brown reaction products. From these products no well defined complex could be isolated. The reason probably is that 1 proved to be an excellent catalyst in the polymerisation of isocyanides\(^6\). Compound 1 appeared to be very hygroscopic and decomposed when brought into contact with even traces of moisture.

Some relevant spectral data of 1 are summarized in the Table. The strongest absorption in the infrared spectrum of solid 1 occurs at around 2218 cm\(^{-1}\); it is assignable to the NC-stretching vibration of the coordinated tert-butyl isocyanide\(^1\). A strong broad absorption around 3377 cm\(^{-1}\) and a medium one around 1607 cm\(^{-1}\) are assignable to the coordinated ethanol\(^7\). The presence of the tert-butyl and of the ethyl group\(^8\) is reflected by sharp, strong to medium absorptions at 2983, 2939, 2927, 2906, 2873, 1476, 1453, 1394, 1372, 1238, and 1198 cm\(^{-1}\). Further sharp, strong to medium absorptions are present at 1074, 1044, 883, 855, and 715 cm\(^{-1}\) besides medium to weak absorptions at 808, 652, 525, 479, 428, and 305 cm\(^{-1}\). A 0.06 molar ethanolic solution of 1 shows a strong NC stretching vibration at 2213.9 cm\(^{-1}\).

The electronic absorptions observed are given in the Table.

The proton magnetic resonance spectrum of 1 in deuterated methanol showed three broad unresolved signals (see Table). From their integrated intensities they could be assigned to the methyl-, methylene-, and tert-butyl group. The corresponding shift values appeared to be very concentration and temperature dependent\(^9\).

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Relevant infrared, electronic, and proton magnetic resonance absorptions of $[\text{NiCl}_2(t\text{-C}_4\text{H}_9\text{NC})(\text{C}_2\text{H}_5\text{OH})]$ (1)

<table>
<thead>
<tr>
<th>Infrared $^a$ cm$^{-1}$</th>
<th>Electronic $^b$ cm$^{-1}$</th>
<th>Proton magnetic resonance ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr-disc</td>
<td>C$_2$H$_5$OH$^b$</td>
<td></td>
</tr>
<tr>
<td>3377 (vOH)</td>
<td>47400</td>
<td>2.54–2.17 (—CH$_3$)</td>
</tr>
<tr>
<td>s; b</td>
<td>[3.59]$^e$</td>
<td>[3]$^f$</td>
</tr>
<tr>
<td>2217.7 (vNC)</td>
<td>35100</td>
<td>4.07–3.96 (t-C$_4$H$_9$)</td>
</tr>
<tr>
<td>vs; sh</td>
<td>[2.49]$^g$</td>
<td>[9]</td>
</tr>
<tr>
<td>1607 (δOH)</td>
<td>24300</td>
<td>6.74–5.75 (—CH$_2$—)</td>
</tr>
<tr>
<td>m; sh</td>
<td>[1.35]$^h$</td>
<td></td>
</tr>
<tr>
<td>428 (vNi-Cl?)$^i$</td>
<td>14500</td>
<td></td>
</tr>
<tr>
<td>w; sh</td>
<td>[0.72]$^i$</td>
<td></td>
</tr>
<tr>
<td>305 (vNi-Cl?)$^i$</td>
<td>w; sh</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ vs very strong, s strong, m medium, w weak; sh sharp, b broad, shl shoulder; range 300–4000 cm$^{-1}$

$^b$ (1–630).10$^{-4}$ molar; room temperature; range 13900–52600 cm$^{-1}$

$^c$ reflectance spectrum; range 12500–47600 cm$^{-1}$

$^d$ 1.22–1.45 molar; $\approx$ 35 °C; TMS as internal standard at 100 MHz

$^e$ log $c$ in brackets; $c$ molar extinction

$^f$ relative integrated intensity in brackets

$^g$ for several nickel dichloride complexes v(Ni-Cl) has been reported to occur in the region 405–289 cm$^{-1}$. See reference 10 and references therein.

At room temperature as well as at $-170$ °C the electron spin resonance spectrum of solid 1 showed a single very broad structureless signal around 249.1 kA/m (3130 oersted), corresponding with a g-value of 2.17. The molar magnetic susceptibility and the magnetic moment of solid 1 at 21 °C appeared to be 64.5. 10$^{-9}$m$^3$mol$^{-1}$ (5.14. 10$^{-5}$ cgau/mol) and 3.48 BM, respectively.

**Discussion**

The simplest structure possible for 1 contains the two neutral ligands as well as the two chloride ions all coordinated to the same nickel(II)

The presence of only one single NC stretching vibration frequency in the infrared spectrum of 1 does not rule out the possibility of an ionic structure like \([\text{Ni}(t\text{-C}_4\text{H}_9\text{NC})_4] [\text{Ni}(\text{C}_2\text{H}_5\text{OH})_4] [\text{NiCl}_4]_2\). However, a square planar arranged \([\text{Ni}(t\text{-C}_4\text{H}_9\text{NC})_4]^{2+}\) ion should absorb around 2245 cm\(^{-1}\), which is a significantly higher wavenumber than 2217.7 cm\(^{-1}\) found for solid 1. A tetrahedral \([\text{Ni}(t\text{-C}_4\text{H}_9\text{NC})_4]^{2+}\) ion should also absorb at a significantly higher wavenumber, viz. at a wavenumber comparable with the value found for the tetrahedral \([\text{Zn}(t\text{-C}_4\text{H}_9\text{NC})_4]^{2+}\) ion. In \([\text{Zn}(t\text{-C}_4\text{H}_9\text{NC})_4] (\text{ClO}_4)_2\) this ion shows a single sharp absorption at 2258 cm\(^{-1}\). Moreover, the electronic spectrum of 1 as a solid as well as in solution showed no evidence for the presence of \([\text{Ni}(\text{C}_2\text{H}_5\text{OH})_4]^{2+}\) or \([\text{NiCl}_4]^{2-}\) ions. Finally an ionic structure is not likely on account of the low conductivity found for ethanolic solutions.

**tert**-Butyl isocyanide and triphenylphosphine are not much separated in the spectrochemical series. If we assume a monomeric pseudo tetrahedral structure for 1 with a carbon atom, an oxygen atom and two chlorine atoms at the apices of a tetrahedron than it seems justifiable to compare 1 with the tetrahedral complexes \([\text{Ni}_2(\text{P(C}_6\text{H}_5)_3)_2\text{Cl}_2]^{16,17}\) and \([\text{Ni}_2(\text{OP(C}_6\text{H}_5)_3)_2\text{Cl}_2]^{18}\), which have a magnetic moment of 3.07 and 3.7 BM, respectively. The intermediate value of 3.48 BM has been found for solid 1. Generally the value of the magnetic moment for pure tetrahedrally coordinated nickel(II) complexes has been found between 3.7 and 4.0 BM. However in 1 symmetry is lower than \(T_d\) or even \(C_{2v}\). The effect of such a symmetry perturbation generally is a substantial lowering of the magnetic moment. The paramagnetic state also follows from the presence of an ESR signal. Moreover it is reflected in the broadness and in the concentration dependency of the NMR absorptions (see also refs. 9 and 20).

In ethanol 1 is monomeric. The following argument shows that also in the solid state a monomeric structure is probably present. An obvious

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polymeric structure has chlorine bridges between two nickel atoms as depicted below.

\[
\begin{array}{c}
\text{NC} & \text{O} \\
\ldots\text{Cl} & \text{Cl} & \ldots\text{Ni} & \ldots\text{Cl} & \text{Cl} \\
\ldots\text{Ni} & \ldots\text{Cl} & \text{Cl} & \ldots\text{Ni} \\
\text{NC} & \text{O} & \ldots\text{NC} & \text{O}
\end{array}
\]

In this case nickel is surrounded by six ligands and one would expect the value of the magnetic moment to be intermediate between 2.9 and 3.3 BM as is generally found for octahedrally coordinated nickel(II)\(^{19,21,22}\). The close similarity of the low intensity bands in the spectra of solid and solution (see Table) also suggests similar coordination chemistry.

At first sight it might appear strange that a neutral monomer like 1 is insoluble in non-electron donor solvents. However, a similar insolubility has been found for olive green \([\text{NiCl}_2\{\text{P(C}_6\text{H}_5\text{)}_3\}_2]\) which by X-ray analysis proved to be monomeric and tetrahedral\(^{16}\).

**Experimental part**

tert-Butyl isocyanide was prepared and purified as described previously.\(^1\) Nickel dichloride hexahydrate (U.C.B., purum) was dehydrated with thionyl chloride\(^{23}\). Dry solvents were stored on molsieve 4A under nitrogen. All manipulations were performed under dry nitrogen.

\[\text{[NiCl}_2(t\text{-C}_4\text{H}_9\text{NC})(\text{C}_2\text{H}_5\text{OH})]\] (1) was prepared at 0 °C by addition of one equivalent of \(t\)-butyl isocyanide to a vigorously stirred 0.24–0.52 molar solution of anhydrous nickel dichloride in absolute ethanol. After five minutes about two thirds of the solvent were removed by vacuum distillation. The remaining concentrated cold reaction mixture was diluted with about half its volume of dry pentane. The resulting pale green precipitate was collected on a glass filter, washed several times with pentane and finally dried at approximately 2 kN/m\(^2\) (15 mm Hg). Yield 60–85 %. Found % (Calcd. %): C 32.5(32.48); H 5.9(5.85); N 5.7(5.41); O 6.5(6.18); Cl 28.2(27.39); and Ni 22.9(22.68).

Upon heating, 1 turned brown at about 100 °C without melting. Anhydrous nickel dichloride was eventually left behind.

The complex is very soluble in methanol and ethanol, slightly soluble in acetone, and insoluble in hydrocarbons and carbon tetrachloride. Chloroform, dichloromethane, acetonitrile and nitromethane decompose the complex.


Ebulliometric molecular weight determinations were performed with a Gallenkamp dual vessel semi-micro Ebulliometer MW125. MW found 278; calculated for the monomer 258.8. Conductivity, $\Lambda_m$, of a 0.06 molar ethanolic solution of I was determined by use of a Philips PR 9500 conductivity bridge at 23°C. Found 8.3 cm$^2$mol$^{-1}$ohm$^{-1}$. Infrared spectra were recorded on a P.E. 457 grating spectrometer; the spectra were calibrated with polystyrene and carbon monoxide$^{24}$. Electronic spectra of solutions were recorded on a Unicam SP 1800 spectrometer and the reflectance spectra on a Shimadzu spectrometer. Proton magnetic resonance spectra were recorded on a Varian HA 100 instrument and the electron spin resonance spectra were run on a Varian EPR V4912 X-band spectrometer.

Magnetic susceptibilities were measured by means of the Faraday force method. For experimental details see reference 25.

Element analysis were carried out under supervision of Mr. W. J. Buis at the Institute for Organic Chemistry TNO at Utrecht.

Acknowledgements

This investigation was partly supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

The authors are indebted to Dr. J. P. Hoekstra for providing and interpreting the magnetic data, to Mr. C. Worrell for recording the ESR spectra, and to Mr. W. A. Pieterson for recording the reflectance spectra.

(Received June 30th, 1972)

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