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Polymorphism of a nickel polymerization catalyst

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Dedicated to Prof. Erker on the occasion of his 60th birthday.

Abstract

Two polymorphs of an highly active nickel(II) salicylaldiminato polymerization catalyst are reported, which to our knowledge represent the first examples of polymorphism of catalytically active polymerization catalysts. The two structures differ significantly in the coordination geometry of the central metal atom. Lattice energy calculations were used to analyze the different solid state structures.

Keywords: Homogeneous catalysis; Solid state structure; Polymorphism; Nickel; N,O-ligands

1. Introduction

For many organic and inorganic compounds different crystal structures, i.e. polymorphic forms, are known. This is of great economic importance since separate patents can be obtained for different polymorphic forms. It is especially important in the field of pharmaceuticals or organic pigments, where it might lead to a prolonged patent protection. In one case Glaxo could maintain the patent for "Zantac" (sales of 3.3 billion US-$ in 1992) for some additional years due to a patent on an (unintentionally formed) polymorphic form, which lasted longer than the patent on the molecule itself [1].

Similar cases are known for organic pigments, where usually an extensive polymorph-screening is conducted [2,3]. While for pharmaceuticals the registration depends on the polymorphic form, an individual registration of polymorphic forms is not necessary for color pigments and fine chemicals. The solid state properties depend on the polymeric form. This is not only true for pigments (for which e.g. color shade and light stability depend on the crystal phase [4]) but also for heterogeneous catalysts, where the catalytic activity may strongly depend on the crystal structure [5–8].

Several studies show that possible crystal structures for simple organic molecules can nowadays be predicted with quite good accuracy [9–14]. But it is almost impossible to decide which of the predicted crystal structures will be formed during an experiment and what procedure leads to one particular polymorphic form [15]. In contrast to organic or inorganic substances much less attention had been paid to the polymorphism of organometallic compounds [16–19] although for certain compounds more than 10 different forms are known [20]. Organometallic compounds are involved as catalysts, precatalysts or intermediates in many homogeneous and heterogeneous processes. Therefore the question of polymorphism may also become

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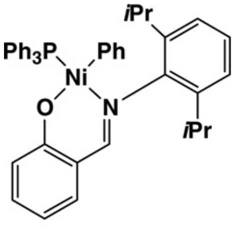

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Fig. 1. Nickel complex **1**.

more and more important in this field. We want to report one example, a nickel(II) polymerization catalyst (**1**, Fig. 1) where we were able to obtain and fully characterize two polymorphic forms.

Since the mid-1990s the area of transition metal catalyzed olefin polymerization was extended by highly active nickel(II) catalysts [21–24]. In his seminal work Brookhart et al. introduced the class of nickel diimine catalyst, which are able to produce linear to highly branched polyethylene [25]. Analogous to metallocenes they are activated by methyl aluminoxane (MAO). In contrast, the Grubbs group later developed new neutral catalyst systems, which in most cases are active without the need for a cocatalyst like MAO. This is a great advantage over the previously known catalysts because now also functionalized monomers can be employed in polymerization reactions [26,27]. This class of neutral, highly active catalysts is based on salicylaldiminato ligands. In our study we investigate one representative of this interesting class of catalysts, which has gotten a lot of attention during the last years [28,29].

2. Results and discussion

Compound **1** could be obtained by the reaction [26] of the sodium salt of the ligand with *trans*-[NiCl(Ph)(PPh$_3$)$_2$], for which we recently developed a straight-forward one-pot synthesis [30]. During our work with **1** we surprisingly found that some of the yellow product obtained from the synthesis changes its color to red over the period of some days. From a crystal growth screening using different solvent systems we succeeded to gain yellow single-crystals (**1**$_{\mathbf{yellow}}$) from slow diffusion of hexane into a concentrated solution in toluene. On the other hand red crystals (**1**$_{\mathbf{red}}$) could be obtained by slow evaporation of a toluene solution. It should be noted, that solutions of **1** show an intense red color. Elemental analysis of both substances showed good agreement with the calculated values. A single crystal analysis of both crystals revealed two polymorphic forms of **1**.

The central coordination geometry is depicted in Fig. 2; important geometric data of both structures are given in Table 1. Two different views from the side (A) and from on top (B) are provided to better describe the differences between the structures.

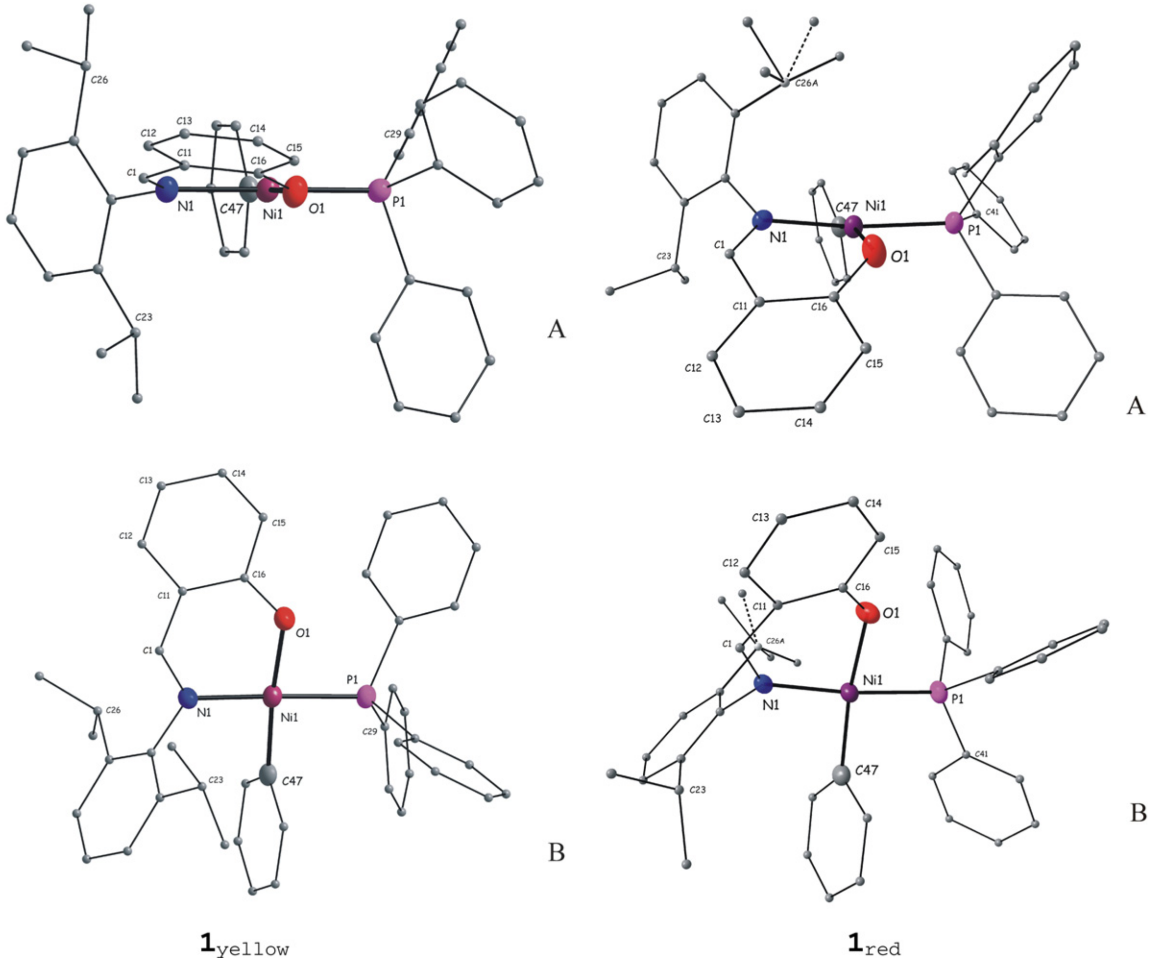
One interesting difference in the solid state structures is a stronger distortion of the square-planar coordination geometry in **1**$_{\mathbf{red}}$. The tendency towards a tetrahedral environment in this structure is obvious from the smaller P–Ni–N– and O–Ni–C angles. Furthermore, the arrangement of the phenolate ring (C11–C16) differs significantly relative to the nickel coordination plane. In **1**$_{\mathbf{yellow}}$ the nickel plane is almost coplanar with the phenolate whereas in **1**$_{\mathbf{red}}$ the salicylaldimine moiety is strongly bent away. The angle between the planes N1–Ni–O1 and O1–C16–C11–C1–N1 differs significantly (red: 31.09(8)°; yellow: 14.3(1)).

Furthermore, one isopropyl group in **1**$_{\mathbf{red}}$ reveals a disorder on two orientations. Lattice energy calculations show that both orientations result in very similar lattice energies, which explains the disorder in the solid state (see Section 4). The polymorphic structures observed herein are best described as conformational polymorphs, since the molecule crystallizes in different conformations [19].

Looking at the molecular conformations in the solid state the question arises if they are simply a consequence of packing effects. In other words, is the formation of the yellow crystal phase from a red solution favorable because of a higher lattice energy? Lattice energy calculations using the software CRYSCA [31] show, that this is not the case. The lattice energy (without intramolecular terms) of the yellow polymorph is about 13 kJ/mol higher than that of the red form (for details see Section 4). This is consistent with the lower density of the yellow form; hence the molecular packing is less efficient.

To get further insight into the thermodynamic properties of both crystal phases we looked at the crystallization behavior of **1**. The yellow crystals grow by slow diffusion of hexane into a concentrated solution of **1** in toluene, whereas the red crystals are formed by slow evaporation from toluene. As noted before, we observed that some of the yellow powder obtained from the synthesis from toluene/hexane turns red after some days. This implies that **1**$_{\mathbf{yellow}}$ is only the metastable kinetic crystallization product. This is converted to the red form if some crystal seeds of the latter are present. This means that **1**$_{\mathbf{red}}$ is the thermodynamically more stable form in the solid state. Solutions of **1** show a deep red color, therefore also in solution the conformation of **1**$_{\mathbf{red}}$ should be present in noticeable amounts.

Aside from the X-ray structure determinations the conformational flexibility is also evident from ^{1}H NMR spectroscopy. Besides the main signals of **1**$_{\mathbf{red}}$ (corresponding to published data [26]) small resonances of a second species are visible (with about 8% intensity from NMR integration). They are strongly shifted to lower field ($\delta = 4.28$ for –CH–, 1.48 and 1.28 ppm for –CH$_3$). Similar results were observed for complexes with halogen substituted ligands [32,33]. A low temperature NMR measurement showed that indeed the second resonances are temperature dependent and presumably caused by **1**$_{\mathbf{yellow}}$. No further resonances are visible in a ^{1}H NMR spectrum at -100 °C in CD$_2$Cl$_2$. This does not change even after warming the NMR tube to RT again for some minutes. The signals of the second species arise only slowly and are not complete



$\mathbf{1}_{\text{yellow}}$ $\mathbf{1}_{\text{red}}$

Fig. 2. Solid-state structure of the yellow ($\mathbf{1}_{\text{yellow}}$; left) and red ($\mathbf{1}_{\text{red}}$; right) polymorphs (A: "side view"; B: "top view"). For clarity only the innermost atoms around the nickel center are given (50% probability). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Comparison of bond length and angles of both polymorphs of **1** (distances in Å, angles in °)

	$\mathbf{1}_{\text{yellow}}$	$\mathbf{1}_{\text{red}}$
Ni1–O1	1.879(2)	1.9059(12)
Ni1–N1	1.948(2)	1.9342(14)
Ni1–C47	1.885(2)	1.901(2)
Ni1–P1	2.1748(6)	2.1833(5)
O1–C16	1.294(3)	1.308(2)
N1–C1	1.295(3)	1.296(2)
N1–C17	1.447(3)	1.440(2)
C1–C11	1.415(3)	1.430(2)
C11–C16	1.405(3)	1.411(3)
Ni1···C23	3.675(3)	4.338(2)
Ni1···C26	4.161(2)	3.347(2)
P1–Ni1–N1	178.57(6)	172.16(4)
P1–Ni1–O1	89.11(5)	85.87(4)
P1–Ni1–C47	85.50(7)	92.17(5)
O1–Ni1–C47	174.54(8)	165.42(6)
O1–Ni1–N1	92.28(8)	91.11(5)
N1–Ni1–C47	93.10(9)	92.54(6)
Ni1–O1–C16	128.59(15)	121.72(11)
N1–Ni1–O1–C16	−20.8(2)	41.40(13)
C47–Ni1–P1–C41	42.14(11)[a]	6.46(9)
P1–Ni1–C47–C52	87.3(2)	79.57(13)

[a] C47–Ni1–P1–C29.

until storing the NMR tube at RT for some days. It is feasible to assume that the second set of signals originates from a second conformation of **1** ($\mathbf{1}_{\text{yellow}}$). Because the equilibrium between both forms is reestablished only slowly the reaction path between both conformations should exhibit a considerable barrier. Unfortunately, due to the strong red color of the solution no change of the color intensity is visible.

3. Conclusion

To the best of our knowledge, this is the first time that polymorphism was found for a highly active nickel polymerization catalyst. We suggest to pay more attention to this phenomenon in the future also in organometallic chemistry.

4. Experimental

Compound **1** was synthesized according to the literature [26]. Crystals of both polymorphic forms were obtained by the procedures described in the main text.

EA:	calculated:	C 76.12%; H 6.21%; N 2.12%
	measured:	C 75.93%; H 6.24%; N 2.06%

5. Lattice energy calculations

Lattice energies were calculated by the program CRYSCA [31]. The energy was calculated by the formula:

$$E = \frac{1}{2}\sum_{i}\sum_{j}\left(-A_{ij}r_{ij}^{-6} + B_{ij}\mathrm{e}^{-C_{ij}r_{ij}}\right)$$

where i stands for the atoms of a reference molecule, and j for all other atoms up to a cut-off radius of 20 Å (which holds for at least 99% of the total van der Waals energy). r_{ij} denotes the interatomic distance. A_{ij}, B_{ij}, and C_{ij} are van der Waals parameters given in Table 2. All parameters not listed in Table 2 were calculated applying the combination rules: $A_{ij} = (A_{ii} \cdot A_{jj})^{1/2}$, $B_{ij} = (B_{ii} \cdot B_{jj})^{1/2}$, $C_{ij} = (C_{ii} + C_{jj})/2$. Actually the choice for the van der Waals parameters of Ni and P does not have a significant effect on the intermolecular energies, since there are no close interactions of Ni and P atoms with any atoms of neighboring molecules.

The intermolecular electrostatic energy is small, since the molecules have a small dipole moment and the surface of the molecules consist of unpolar groups only. The molecular packing is determined by van der Waals interactions. Hence the intermolecular electrostatic energy could be neglected in the lattice energy calculations.

The lattice energy minimizations started from the experimental crystal structures of the yellow and red polymorphs. Hydrogen atom positions were calculated with C–H distances of 1.04 Å. Since we were interested in the intermolecular energies, we fixed the intramolecular structure and optimized only lattice parameters, position, and spatial orientation of the molecules. The crystal symmetry was maintained in all calculations.

In the red polymorph one isopropyl group is disordered over two orientations; separate calculations were performed with both orientations. The resulting lattice energies were −239.9 and −239.1 kJ/mol. This small difference explains the observed disorder in the solid state. The lattice energy of the yellow phase was calculated to be −227.2 kJ/mol, i.e. the energy is less favorable by about 13 kJ/mol.

Table 2
Van der Waals parameters [9,10]

Atoms	A_{ij} (kJ mol^{-1} Å^6)	B_{ij} (kJ mol^{-1})	C_{ij} (Å^{-1})
H···H	144.2	11104	3.74
H···C	523	36677	3.67
C···C	2377	349908	3.60
N···N	1240.7	201191	3.78
O···O	1242.6	372203	4.18
P···P	6000	1000000	3.56
Ni···Ni	6463	1804000	4.00

In additional calculations, intramolecular degrees of freedom (rotations around single bonds; bending of the salicylaldimine fragment) were included in the optimization. The energy difference between the yellow and the red polymorph did not decrease.

In all cases the crystal structure did not change significantly upon optimization: the mean changes were below 1% for the lattice parameters, about 0.1 Å for the molecular position and about 1° for the orientation of the molecules. This confirms that the applied force field is well suitable for this compound.

6. Single crystal X-ray structure determination of compounds $\mathbf{1}_{\mathbf{yellow}}$ and $\mathbf{1}_{\mathbf{red}}$

Crystal data and details of the structure determination are presented in Table 3. Suitable single-crystals for the X-ray diffraction studies were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3,

Table 3
Crystallographic data for $\mathbf{1}_{\mathbf{yellow}}$ and $\mathbf{1}_{\mathbf{red}}$

	$\mathbf{1}_{\mathbf{yellow}}$	$\mathbf{1}_{\mathbf{red}}$
Formula	$C_{43}H_{42}NNiOP$	$C_{43}H_{42}NNiOP$
Fw	678.44	678.44
Color/habit	Yellow/fragment	Red/needle
Crystal dimensions (mm^3)	0.08 × 0.25 × 0.31	0.18 × 0.25 × 0.51
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	11.2782(2)	22.2976(2)
b (Å)	11.4583(2)	14.1798(1)
c (Å)	14.6318(2)	11.0570(1)
α (°)	85.1577(8)	90
β (°)	70.7085(7)	99.8589(3)
γ (°)	82.1269(5)	90
V (Å^3)	1766.31(5)	3444.33(5)
Z	2	4
T (K)	163	163
D_{calcd} (g cm^{-3})	1.276	1.308
μ (mm^{-1})	0.629	0.645
F(000)	716	1432
Θ range (°)	1.48–25.30	1.71–25.35
Index ranges (h,k,l)	±13, ±13, ±17	±26, ±17, ±13
Number of independent reflections	6413	6313
Number of observed reflections [$I > 2\sigma(I)$]	4685	5444
Number of data/restraints/parameters	6413/0/592	6313/0/587
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0399/0.0798	0.0300/0.0725
R_1/wR_2 (all data)[a]	0.0700/0.0888	0.0399/0.0769
Goodness-of-fit (on F^2)[a]	1.033	1.017
Largest difference in peak and hole (e Å^{-3})	+0.38/−0.28	+0.23/−0.41

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(n-p)\}^{1/2}$.

κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collections were performed at low temperatures (OXFORD CRYOSYSTEMS cooling device). Each crystal was measured with a couple of data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.5/1.0°$. Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms could be located in the final difference Fourier maps and were allowed to refine freely with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o{}^2 - F_c{}^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.002. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium *4* PC, with the WINGX system, including the programs DIAMOND, PLATON, SHELXL-97, and SIR92 [34–41].

Specials. $\mathbf{1_{red}}$: A disorder over two positions observed for one isopropyl group [C26; 0.506(8)/0.494(8)] could be resolved and modeled clearly. For the disordered carbon atoms methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{\text{C–H}} = 0.98$ Å and $U_{\text{iso (H)}} = 1.5U_{\text{eq(C)}}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene $d_{\text{C–H}}$ distances of 1.00 Å, and $U_{\text{iso(H)}} = 1.2U_{\text{eq(C)}}$.

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Appendix A. Supplementary material

CCDC 641778 and 641777 contain the supplementary crystallographic data for $\mathbf{1_{yellow}}$ and $\mathbf{1_{red}}$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.070.

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