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[*N*-({(*R*)-2-[(*N*-Benzylprolyl)amino]phenyl}-phenylmethylene)-2(*S*)-(pent-4-enyl)-glycinato]nickel(II)

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.048
wR factor = 0.082
Data-to-parameter ratio = 16.6

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

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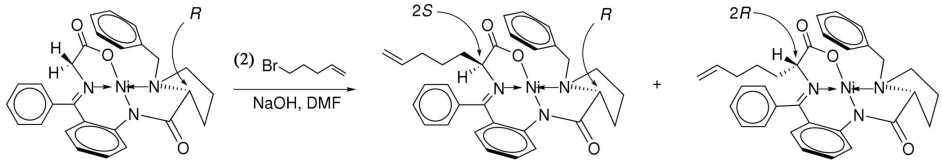
The title compound, [Ni($C_{32}H_{33}N_3O_3$)], crystallized as a minor product during the purification of its 2(*R*)-pent-4-enyl diastereomer. Mixtures of the title compound and its enantiomer self-resolve.

Comment

ω-Unsaturated amino acids are of value in terms of their biological importance and their utility as asymmetric synthetic building blocks (Rutjes *et al.*, 2000). The double bond is a masked functional group and can be easily transferred to ω-hydroxyl, ω-halogen, ω-epoxy, ω-amino, aldehyde, and carboxyl amino acids (Reetz, 1999). In the course of our ongoing [3.3.0]-, [3.4.0]- and [3.5.0]bicyclic β-turn dipeptide-inserted biologically active peptide syntheses (Gu *et al.*, 2005), a practical large-scale synthesis of enantiomerically pure ω-unsaturated amino acids has become necessary. For this purpose, we have developed an alkylation–hydrolysis two-step strategy, shown in Fig. 1, for the *R* enantiomer using the Gly Ni—*R*-2-[*N*-(*N*′-benzylprolyl)amino]benzophenone (BPB) complex (Gu *et al.*, 2004; Belokon *et al.*, 1998), in which fractional crystallization plays a critical role. Thus, allyl glycine and but-3-enylglycine nickel(II) complex major products can be purified by the products mixture by recrystallization from dichloromethane and diethyl ether. However, during the purification of the (*R*)-pent-4-enyl-glycine-nickel(II)–(*R*)-BPB complex, the minor product, (3) (title compound), crystallized out first, and the mother liquor became a solution of the pure major product (4).



(1) *R*-Ni(II)-complex (3) *R*(2*S*)-minor (4) *R*(2*R*)-major

The structure of (3) is shown in Fig. 1. The configurations of C6 and C31 were found to be *R* and S, respectively, in contrast to the two *R* configurations of (4). Another interesting point regarding the crystallization of this compound is that a racemic mixture made of (3) and its enantiomer self-resolve, producing crystals which are identical to those obtained from solutions of the enantiomerically pure compounds (Carducci *et al.*, 2006).

Experimental

The synthesis of the title compound, (3), was accomplished starting with Gly Ni-(*R*)-2-[*N*-(*N*′-benzylprolyl)amino]benzophenone com-

plex (1), which was synthesized from (*R*)-proline in three steps (Belokon *et al.*, 1998). Ni^{II} complex (1) (10 g, 20 mmol) and ground NaOH (8 g, 200 mmol) were added to a flask which was purged twice with argon. Anhydrous DMF (80 ml) was added by syringe, and the mixture was allowed to react for 5 min at room temperature before 5-bromo-1-pentene (2.3 ml, 19.4 mmol) was added in one portion. The reaction was then kept at room temperature for another 5 min. The solution was decanted into an aqueous solution (800 ml) containing 5% of acetic acid. The suspension was dissolved in benzene (800 ml) and the emulsion was diminished by filtration through Celite. The benzene solution was washed with brine (4 × 800 ml), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The sample was loaded on a short column, and flash column chromatography employed a gradient of acetone in dichloromethane (2 to 40%) to afford a mixture of diastereomeric Ni^{II} complex products (3) and (4) (96% combined yield). The solution was concentrated under reduced pressure, and the residue was dissolved in a small amount of dichloromethane. Diethyl ether was added slowly until a small amount of precipitation was observed. Dichloromethane (1–2 ml) was then added, and the solvents were allowed to slowly evaporate from the open flask overnight. The purple minor product crystal (3) was collected (9% yield; m.p. 523 K).

Crystal data

$[Ni(C_{32}H_{33}N_3O_3)]$	$Z = 4$
$M_r = 566.32$	$D_x = 1.418$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.8595$ (9) Å	$\mu = 0.77$ mm^{-1}
$b = 14.6480$ (14) Å	$T = 173$ (2) K
$c = 18.3738$ (17) Å	Plate, orange
$V = 2653.6$ (4) Å^3	0.26 × 0.19 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer	38303 measured reflections
	6366 independent reflections
φ and ω scans	5252 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$R_{int} = 0.070$
	$\theta_{max} = 28.0°$
$T_{min} = 0.825$, $T_{max} = 0.963$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.082$	$\Delta\rho_{max} = 0.91$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
6366 reflections	Absolute structure: Flack (1983), 2752 Friedel pairs
383 parameters	
H-atom parameters constrained	Flack parameter: 0.002 (11)

H atoms were included at idealized positions although many could be found in a difference map. They were constrained to ride on their carrier atoms [U_{iso}(H) = 1.2U_{eq}(carrier atom) or 1.5U_{eq}(carrier atom) and C—H = 0.95–1.00 Å]. A rigid bond restraint was applied to all atoms such that components of the displacement parameters in the direction of the bond were restrained to be equal within an s.u. of 0.01. There is rotational disorder present in the phenyl ring containing atoms C8–C13, which was resolved by splitting the ring into two parts and applying a similarity restraint to the U^{ij} components of atoms within 1.7 Å of each other. The population of each component was allowed to vary and refined to a value of 0.58 (2) for component B.

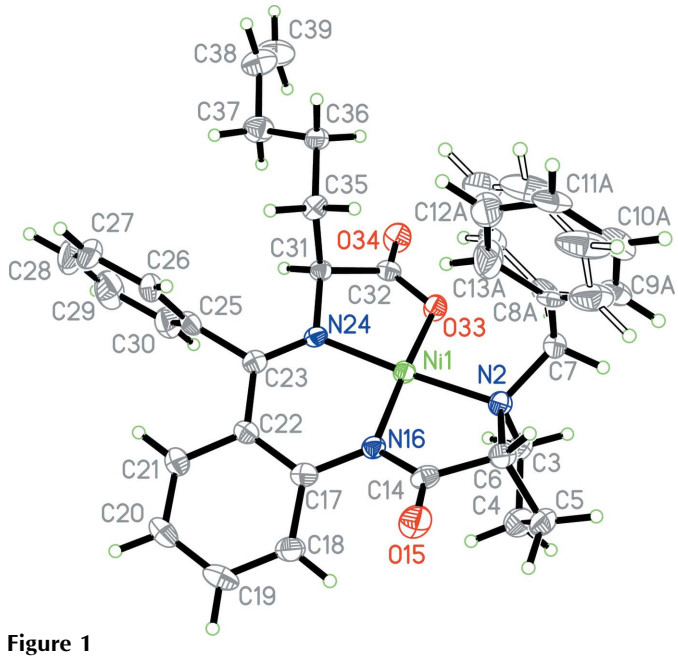


Figure 1
The title molecular structure, with 50% probability displacement ellipsoids. Both disorder components are shown.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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