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Preparation of an enantiomerically pure helical nickel(II) complex using a new chiral tetradentate ligand derived from an industrial waste material†

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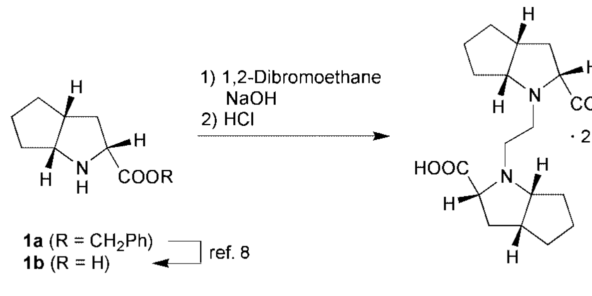
Received 16th March 2000, Accepted 31st May 2000

A new tetradentate ligand (all-*R*)-1,2-bis(2-aza-3-carboxybicyclo[3.3.0]octan-2-yl)ethane (H_2baboc) derived from an industrial waste material has been used as an asymmetric complexing agent for the transition metal nickel(II). The enantiomerically pure complex [Ni(baboc)(H_2O)]·H_2O has been prepared and its crystal structure has been determined by X-ray diffraction. According to the τ criterion the pentagonal co-ordination sphere for Ni^{II} is identified as square pyramidal.

Introduction

The wide use of chiral tetradentate ligands is mainly based on their successful application in several fields of organometallic chemistry *e.g.* enantioselective catalysis[2,3] or ligand exchange chromatography.[4] As a preferred steric framework of this type of complexing agents, C_2-symmetrical structures have been shown to be most efficient.[5] Consequently, a challenging endeavour in this field is the development of easily available, economical and cheap C_2-symmetrical tetradentate precursor systems, which can be regarded as starting materials for a broad variety of new classes of C_2-symmetrical compounds.

In the context of our studies on the utilization[1,3,6] of the non-recyclable enantiomerically pure waste material **1a**[7] from the production of the ACE-inhibitor ramipril by Hoechst AG, we now wish to report the synthesis of a novel, enantiomerically pure tetradentate and C_2-symmetrical ligand H_2baboc **2** (Scheme 1). Since the design of new asymmetric catalysts needs knowledge about the complexing behaviour of the ligand systems, we decided to prepare and isolate a transition metal complex based on chiral **2**. In this paper we describe investigations concerning the properties of **2** as a complexing agent towards Ni^{II} and report the asymmetric formation and crystal structure of a five-co-ordinated nickel(II) complex containing **2**.



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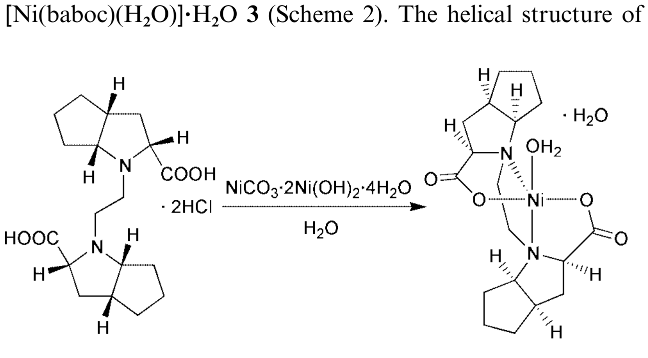
Scheme 1 Synthesis of the edda analogue **2** starting from the α-amino acid **1b**.

Results and discussion

The C_2-symmetrical, optically active compound H_2baboc **2** was prepared from the α-amino acid **1b** which is obtained by a Pd/C-catalysed hydrogenation of the benzyl ester **1a**.[8] The conversion of **1b** with 1,2-dibromoethane under basic conditions led to ligand **2** in 55% chemical yield (Scheme 1). In this connection, **2** can be regarded as a new chiral analogue of the efficient well known achiral edda (*e*thylene*d*initrilo*dia*cetate) ligand.[9] Owing to the derivatizing potential of its carboxylic functions, the ligand **2** also represents a new multifunctional precursor system for a broad variety of C_2-symmetrical ligands. Accordingly, modifying these carboxylic groups offers a convenient access to the corresponding tetramines and bis(aminoalcohol) derivatives, which, in part, already have been applied in asymmetric catalysis.[3,10] In addition, we were pleased to find that **2** itself shows an interesting complexing behaviour towards the nickel(II) ion.

Thus, refluxing compound **2** with two equivalents of basic nickel(II) carbonate in water followed by filtration from insoluble nickel hydroxide and slow crystallization from water results in the formation of deep green, cubic crystals of [Ni(baboc)(H_2O)]·H_2O **3** (Scheme 2). The helical structure of **3** contains the tetradentate ligand **2**. Therein both secondary amine and carboxylic donor groups, respectively, are attached to the central nickel(II) (see crystal structure in Fig. 1). In addition, a water molecule is co-ordinated *via* its nucleophilic oxygen atom. The substance crystallized with a further



2 **3**

Scheme 2 Synthesis of the nickel(II) complex **3**.

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† Utilization of industrial waste materials. Part 19. For Part 18 see ref. 1.

DOI: 10.1039/b002130j

Table 1 Selected bond angles (°) of the nickel(II) complex **3**

O(3)–Ni(1)–O(5W)	90.21(12)	C(6)–C(7)–C(11)	102.3(3)
O(3)–Ni(1)–O(1)	165.70(13)	C(9)–C(8)–C(7)	106.1(4)
O(5W)–Ni(1)–O(1)	88.75(12)	C(8)–C(9)–C(10)	107.9(4)
O(3)–Ni(1)–N(3)	92.35(11)	C(9)–C(10)–C(11)	106.3(4)
O(5W)–Ni(1)–N(3)	157.23(15)	N(3)–C(11)–C(7)	107.4(3)
O(1)–Ni(1)–N(3)	83.25(11)	N(3)–C(11)–C(10)	113.6(3)
O(3)–Ni(1)–N(12)	84.64(10)	C(7)–C(11)–C(10)	104.3(3)
O(5W)–Ni(1)–N(12)	114.87(16)	C(1)–N(12)–C(13)	113.1(3)
O(1)–Ni(1)–N(12)	108.69(13)	C(1)–N(12)–C(20)	108.1(3)
N(3)–Ni(1)–N(12)	87.89(12)	C(13)–N(12)–C(20)	104.3(3)
C(5)–O(1)–Ni(1)	117.3(2)	C(1)–N(12)–Ni(1)	103.0(2)
C(14)–O(3)–Ni(1)	115.6(2)	C(13)–N(12)–Ni(1)	103.62(19)
N(12)–C(1)–C(2)	113.0(3)	C(20)–N(12)–Ni(1)	124.9(2)
N(3)–C(2)–C(1)	109.3(3)	N(12)–C(13)–C(15)	103.5(3)
C(11)–N(3)–C(2)	111.3(3)	N(12)–C(13)–C(14)	113.6(3)
C(11)–N(3)–C(4)	106.4(3)	C(15)–C(13)–C(14)	109.1(3)
C(2)–N(3)–C(4)	111.5(3)	O(4)–C(14)–O(3)	124.5(3)
C(11)–N(3)–Ni(1)	114.6(2)	O(4)–C(14)–C(13)	118.0(3)
C(2)–N(3)–Ni(1)	104.2(2)	O(3)–C(14)–C(13)	117.4(3)
C(4)–N(3)–Ni(1)	109.0(2)	C(13)–C(15)–C(16)	104.4(3)
N(3)–C(4)–C(5)	112.0(3)	C(15)–C(16)–C(20)	105.2(3)
N(3)–C(4)–C(6)	106.9(3)	C(15)–C(16)–C(17)	116.8(4)
C(5)–C(4)–C(6)	111.9(3)	C(20)–C(16)–C(17)	105.9(4)
O(2)–C(5)–O(1)	123.8(4)	C(18)–C(17)–C(16)	105.1(5)
O(2)–C(5)–C(4)	118.7(3)	C(19)–C(18)–C(17)	110.2(6)
O(1)–C(5)–C(4)	117.4(3)	C(18)–C(19)–C(20)	105.7(4)
C(7)–C(6)–C(4)	106.8(3)	C(19)–C(20)–N(12)	115.1(4)
C(8)–C(7)–C(6)	115.0(4)	C(19)–C(20)–C(16)	106.7(4)
C(8)–C(7)–C(11)	104.6(3)	N(12)–C(20)–C(16)	106.8(3)

Table 2 Selected bond lengths (pm) of complex **3**

Ni(1)–O(3)	198.5(2)	C(6)–C(7)	152.3(6)
Ni(1)–O(5W)	199.5(3)	C(7)–C(8)	151.8(7)
Ni(1)–O(1)	199.6(3)	C(7)–C(11)	153.7(5)
Ni(1)–N(3)	205.7(3)	C(8)–C(9)	149.4(8)
Ni(1)–N(12)	211.4(3)	C(9)–C(10)	152.5(7)
O(1)–C(5)	126.6(5)	C(10)–C(11)	154.2(6)
O(2)–C(5)	122.7(5)	N(12)–C(13)	150.2(4)
O(3)–C(14)	127.3(5)	N(12)–C(20)	152.3(4)
O(4)–C(14)	124.0(4)	C(13)–C(15)	152.4(5)
C(1)–N(12)	148.3(4)	C(13)–C(14)	152.7(5)
C(1)–C(2)	152.3(5)	C(15)–C(16)	152.6(5)
C(2)–N(3)	149.4(4)	C(16)–C(20)	153.5(6)
N(3)–C(11)	148.8(4)	C(16)–C(17)	153.6(7)
N(3)–C(4)	150.6(4)	C(17)–C(18)	146.2(11)
C(4)–C(5)	152.8(5)	C(18)–C(19)	145.7(9)
C(4)–C(6)	154.1(6)	C(19)–C(20)	152.0(6)

molecule of water in its lattice. This crystal water H_2O(6w) is linked by a hydrogen bond (265.7 pm) to the ligand water H_2O(5w).

In order to clarify the pentagonal co-ordination sphere at the nickel(II) ion as square pyramidal or trigonal bipyramidal, the corresponding τ criterion[11] was checked, where $\tau = (\beta - \alpha)/60$ with β as the largest and α as second-largest bond angle of the complex (perfectly square pyramidal geometry, $\tau = 0$; perfectly trigonal bipyramidal geometry, $\tau = 1$). The calculated value $\tau = 0.15$ consequently reveals a nearly square pyramidal structure of the nickel(II) complex **3**.

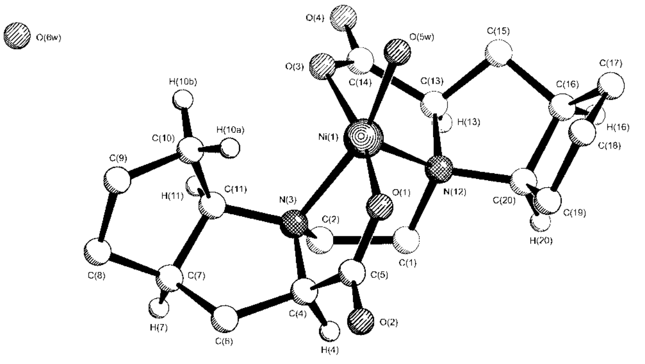
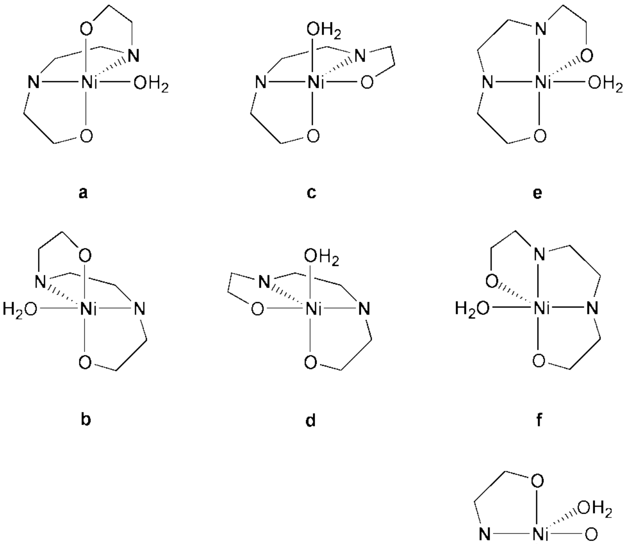


Fig. 1 Crystal structure of the nickel(II) complex **3**.

In the crystal structure of [Ni(baboc)(H_2O)]·H_2O **3** (Fig. 1, Tables 1–3) the observed lengths of the O–Ni bonds, including O(5w)–Ni, are all similar and vary between 198.5(2) and 199.6(3) pm. The opposite is true for the N–Ni bonds. There is a difference of 5.7 pm between the N(3)–Ni bond (205.7(3) pm) in the square plane and the N(12)–Ni bond (211.4(3) pm) at the top of the pyramid. The bond angles between nickel(II) and the adjacent *cis*-co-ordinated heteroatoms (nitrogen and oxygen atoms) were *ca.* 90°, typical for square pyramids, with the exception of O(1)–Ni–N(3). This additionally confirmed the square pyramidal structure of the optically active complex **3**. Therefore, nickel(II) is situated above the best plane defined by the four atoms N(3), O(3), O(5w) and O(1). Furthermore, the free co-ordination site at the bottom of the complex is partially shielded by the annellated cyclopentane system C(7)–C(8)–C(9)–C(10)–C(11), in particular by the two hydrogens H(10a) and H(10b). This is confirmed by a comparison with the edda ligand.[12] In the latter case there is no shielding of this position. Therefore the co-ordination of one further water molecule leads here to an octahedral geometry.

With regard to their conformations the three five-membered chelate rings show distinct deviations. As illustrated by the torsion angles (Table 3), the chelate ring Ni(1)–O(1)–C(5)–C(4)–N(3) is almost planar. In contrast to this the ring Ni(1)–N(3)–C(2)–C(1)–N(12) shows considerable distortions. In addition the ring Ni(1)–O(3)–C(14)–C(13)–N(12) favours an envelope conformation.

In the nickel(II) complex **3** the inner, sterically hindered tetradentate ligand leads to a significant stereoselective arrangement at the Ni (which is usually labile to metal–ligand exchange). As shown in Fig. 1 the two oxygen atoms O(1) and O(3) adjacent to the central nickel(II) are *trans*-co-ordinated. Regarding the stereochemistry determined by the nitrogen atoms N(3) and N(12) and the corresponding α-C atoms C(2) and C(1), a left-handed helix is obtained as depicted in Scheme 3 (structure **a**). The existence of another *trans* complex (structure **b**) as well as the analogous *cis* stereoisomers (structures **c**–**g**) were not observed in the isolated crystalline product **3**, but some of those additional structures might exist in solution because of the lability of nickel(II) compounds.



Scheme 3 Possible isomeric forms of complex **3**.

Table 3 Selected torsion angles (°) of complex **3**

Ni(1)–O(1)–C(5)–C(4)	−4.1(5)	C(2)–C(1)–N(12)–Ni(1)	34.7(3)
N(3)–Ni(1)–O(1)–C(5)	7.7(3)	N(3)–C(2)–C(1)–N(12)	−55.0(4)
C(4)–N(3)–Ni(1)–O(1)	−9.0(2)	Ni(1)–O(3)–C(14)–C(13)	−4.3(4)
C(5)–C(4)–N(3)–Ni(1)	9.4(3)	N(12)–Ni(1)–O(3)–C(14)	−8.2(3)
O(1)–C(5)–C(4)–N(3)	−4.0(5)	C(13)–N(12)–Ni(1)–O(3)	17.5(2)
Ni(1)–N(3)–C(2)–C(1)	42.4(3)	C(14)–C(13)–N(12)–Ni(1)	−24.0(3)
N(12)–Ni(1)–N(3)–C(2)	−19.0(2)	O(3)–C(14)–C(13)–N(12)	20.7(4)
C(1)–N(12)–Ni(1)–N(3)	−8.0(2)		

Conclusion

In conclusion, this paper presents one of the rare examples of an enantiomerically pure, helical nickel(II) complex, which was prepared starting from the new tetradentate ligand **2**. Thus, we not only developed a novel ligand system **2** which can further serve as a precursor for a broad variety of ligand families, but also demonstrated its complexing ability towards a transition metal ion, namely Ni^{II}. From the X-ray analysis of **3**, we gained insight into the well defined structure of such a type of complex. Comparison with the octahedral complex [Ni(edda)-$(H_2O)_2$]·H_2O[12] points out that the steric influence of the chiral bicyclic system is responsible for the detected square pyramidal geometry. The structural information should be helpful for the design of new transition metal complexes based on **2** or derivatives thereof.

Experimental

Melting points (uncorrected) were determined in a Linström apparatus. Infrared spectra were recorded using a Beckman IR 4220 spectrometer as KBr discs for solids, ^1H and ^{13}C NMR spectra on a Bruker AM 300 spectrometer (300 MHz). Optical rotations were measured with a Perkin-Elmer polarimeter 241 MC, mass spectra with a Finnigan-MAT 212 (datasystem SS 300) spectrometer. The waste material (all-*R*)-2-azabicyclo-[3.3.0]octane-3-carboxylic acid benzyl ester **1a**[7] was obtained from Hoechst AG.

Preparations

(all-*R*)-1,2-Bis(2-aza-3-carboxybicyclo[3.3.0]octan-2-yl)-ethane dihydrochloride H$_2$baboc·2HCl 2. After dissolving compound **1b**[8] (15.5 g; 100 mmol) in aqueous NaOH (27 ml; 4.5 M), the solution was refluxed and treated with 1,2-dibromoethane (9.4 g; 50 mmol) and potassium carbonate (6.90 g). The mixture was refluxed for 3 h, cooled to room temperature and acidified with concentrated hydrochloric acid to pH 5. The resulting deep green mixture was filtered, evaporated *in vacuo*, and the residue dissolved in methanol. Further filtration from the inorganic salts and subsequent concentration (to a volume of 30 ml), followed by treatment with diethyl ether under stirring gave the product as a colourless, amorphous solid. Further recrystallization from Pr^{i}OH and water gave **2** as colourless needles, yield 12.18 g (55%), mp 221 °C (decomposition), $[\alpha]_D^{20} = +34.9$ ($c = 1.00$, MeOH) (Found: C, 48.39; H, 7.80; N, 6.21. $C_{18}H_{34}Cl_2N_2O_6 \cdot 2H_2O$ requires C, 48.54; H, 7.69; N, 6.29%), $\tilde{\nu}_{max}$/cm^{-1} (OH) 3700br and (C=O) 1720s (KBr); $\delta_H(D_2O)$ 1.30–1.45, 1.52–1.78, 1.94–2.05 (3m, 4 H + 6 H + 4 H, H5′, H5″, 2 × H6′, 2 × H6″, 2 × H7′, 2 × H7″, 2 × H8′, 2 × H8″), 2.55–2.68 (m, 2 H, H4′, H4″), 2.76–2.90 (m, 2 H, H4′, H4″), 3.32–3.58 (m, 4 H, 2 × H1, 2 × H2), 3.82–3.90 (m, 2 H, H1′, H1″) and 3.96 (dd, $J = 7.8$, 10.7 Hz, 2 H, H3′, H3″); $\delta_C(D_2O)$ 23.6, 28.8, 31.3, 36.1 [C4′, C4″, C6′, C6″, C7′, C7″, C8′, C8″], 42.0 [C5′, C5″], 51.0 [C1, C2], 70.2, 78.1 [C3′, C3″, C1′, C1″] and 174.0 [2 × CO_2H]; *m*/*z* (CI, isobutane) 337 ($MH^+ - 2HCl$), 293 ($MH^+ - 2HCl - CO_2$) and 249 ($MH^+ - 2HCl - 2CO_2$).

[Ni(baboc)(H$_2$O)]·H$_2$O 3. The compound $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (1.88 g; 5 mmol) was added to a solution of **2** (3.36 g; 10 mmol) in 100 ml of water. The deep green reaction mixture was refluxed and subsequently treated with further amounts of water to dissolve insoluble nickel salts. After addition of about 800 ml water the reaction mixture was evaporated *in vacuo* to dryness. The solid residue was recrystallized from water, followed by slow evaporation of the solvent at room temperature and atmosphere pressure to obtain deep green, cubic crystals of the nickel(II) complex **3** (1.46 g, 34%), mp >174 °C (decomposition; thereby, the green colour disappears), $[\alpha]_D^{20} = -169.1$ ($c = 1.15$, MeOH) (Found: Ni, 13.94. $C_{18}H_{28}N_2NiO_5 \cdot H_2O$ requires Ni, 13.68%); $\tilde{\nu}_{max}$/cm^{-1} (OH) 3150br and (C=O) 1620s (KBr).

Crystallography

Data for complex **3** were recorded at 295 K on a Siemens STOE AED 2 diffractometer using graphite-monochromated Mo-Kα radiation. The crystal structure was solved by direct methods using the SHELXTL PLUS program package. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. In the final cycles of the refinement based on 243 variable parameters the hydrogens were included at calculated positions according to the riding model with $U = 8$ pm^2 as the fixed isotropic displacement parameter.

Crystal data. $C_{18}H_{30}N_2NiO_6$, $M = 429.1$, monoclinic, space group $P2_1$, $a = 730.20(10)$, $b = 1521.60(10)$, $c = 892.50(10)$ pm, $U = 958.47(10) \times 10^6$ pm^3, $\beta = 104.860(10)$°, $Z = 2$, $\mu = 1.049$ mm^{-1}, reflections collected 2336, independent reflections 2172 ($R_{int} = 0.0272$), observed reflections 2104 ($I > 2\sigma(I)$), $R1 = 0.0349$, $wR2 = 0.0910$ (obs. data), $R1 = 0.0361$, $wR2 = 0.0919$ (all data).

CCDC reference number 186/2018.

See http://www.rsc.org/suppdata/dt/b0/b002130j/ for crystallographic files in .cif format.

Acknowledgements

The authors thank Hoechst AG for their generous gift of chemicals.

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