

A Distinct Tetradentate N₂O₂-type Ligand: (*o*-Carboranyl)bis(2-hydroxymethyl)pyridine

Florencia Di Salvo,^[a,b] Francesc Teixidor,^[a] Clara Viñas,^[a] and José Giner Planas*^[a]

Dedicated to Professor Heinrich Nöth on the Occasion of His 85th Birthday

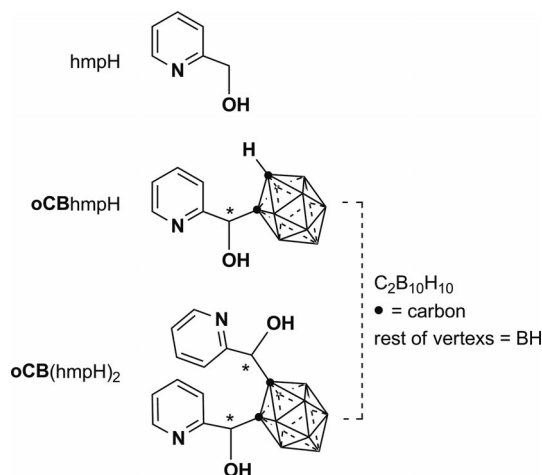
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Abstract. A new chiral racemic ligand (*o*-carboranyl)bis(2-hydroxymethyl)pyridine **oCB(hmpH)**₂, that is composed of a central *o*-carborane unit where two arms radiate out of the cluster carbons each one containing a 2-pyridylmethylalcohol chelating arms, provides two potentially bidentate {NO} or one tetradentate {N₂O₂} binding pockets. An unprecedented octahedral Co^{II} complex [CoCl₂(*anti*-**oCB(hmpH)**₂)] was obtained under aerobic conditions and charac-

terized by X-ray crystallography as well as IR and NMR spectroscopy. *anti*-**oCB(hmpH)**₂ acts as a tetradentate N₂O₂-ligand affording the complex as a racemic mixture of *cis-α* Δ-[CoCl₂(^{RR}*anti*-**oCB(hmpH)**₂)] and Λ-[CoCl₂(^{SS}*anti*-**oCB(hmpH)**₂)]. The new ligand **oCB(hmpH)**₂ appears to be suitable for producing a variety of new chiral-at-metal complexes.

Introduction

In recent decades, the design of hybrid functional materials has been a matter of special interest because of their potential applications in a number of areas.^[1] A well-known approach for the preparation of such systems is the synthesis of organic-inorganic frameworks where transition metal ions and nitrogen containing heterocyclic ligands have proved useful for the construction of solid-state architectures and inorganic crystal engineering.^[2] In particular, pyridyl based ligands have been successfully used for constructing a wide array of architectures with applications ranging from gas storage in porous frameworks to novel luminescence or magnetic materials.^[3] The increasing need for evolved systems and demanding assemblies has led to the emergence of hetero-donating functions,^[3a,f] among which *N,O* ligands such as (2-hydroxymethyl)pyridine (**hmpH**) are candidates (Scheme 1, top). These simple alcohol pyridines have proved to be successful building blocks for the self-assembly of metallosupramolecular architectures with exciting physical properties.^[4] We have recently described the synthesis, molecular and supramolecular characterization of a series of chiral nitrogenated aromatic carboranyl alcohols such as e.g., (*o*-carboranyl)(2-hydroxymethyl)pyridine (**oCBhmpH**)



Scheme 1.

as shown in Scheme 1.^[5] The latter can be regarded as a **hmpH** ligand where one of the hydrogen atoms at the -CH₂- position of the alcohol arm has been replaced by a carboranyl (*closo*-1,2-C₂B₁₀H₁₀) fragment. The high thermal and chemical stability, hydrophobicity, acceptor character, ease of functionalization and three-dimensional nature of the icosahedral carborane clusters make these new molecules valuable ligands in coordination chemistry and we recently published the first results on the metallosupramolecular chemistry of these ligands.^[6] Thus, **oCBhmpH** acts as a bidentate *N,O*-ligand, giving an octahedrally coordinated Co^{II} complex [CoCl₂(**oCBhmpH**)₂] and providing an interesting intrinsically porous molecular material, which porosity is triggered by self-assembly into the solid state and by the presence of the carboranyl fragment. In our continuing exploration of the synthetic and structural chemis-

* Dr. J. G. Planas
Fax: +34-93-580-57-29
E-mail: jginerplanas@icmab.es

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)
Campus U.A.B.
08193 Bellaterra, Spain

[b] Current Address: Departamento de Química Inorgánica, Analítica, y Química Física
Facultad de Ciencias Exactas y Naturales
Universidad de Buenos Aires, INQUIMAE-CONICET
Ciudad Universitaria, Pabellón 2
C1428EHA Buenos Aires, Argentina

try of the *o*-carboranyl alcohols we have just synthesized a whole family of disubstituted *o*-carboranylalcohols, including **oCB(hmpH)₂** (Scheme 1, bottom).^[7] Those constitute a second generation of compounds where two arms radiate out of the cluster carbon atoms each containing a pyridyl or quinolylmethylalcohol with a chiral carbon atom. The presence of two chelating arms, provides two potentially bidentate {NO} or one tetradentate {N₂O₂} binding pockets. Following our first results on the metallosupramolecular chemistry of the monosubstituted *o*-carboranylalcohol ligands,^[6] we have already initiated a systematic study of the metallosupramolecular chemistry of all these new disubstituted ligands with several transition metals. In this paper we report the synthesis, characterization and molecular structure of the first metal complex with this new type of disubstituted *o*-carboranylalcohols ligand **oCB(hmpH)₂**, which corresponds to a mononuclear octahedral Co^{II} complex.

Results and Discussion

As mentioned in the introduction, we are interested in the coordination chemistry of the new disubstituted carboranylalcohols and we have concentrated our attention on the 2-pyridine derivative **oCB(hmpH)₂** shown in Scheme 1. The latter may act as a bis-bidentate N,O- or tetradentate N₂O₂-ligand in molecular complexes. In addition to that, **oCB(hmpH)** contains two chiral centers that can adopt either *R* or *S* configuration and therefore lead to the formation of two diastereoisomers, a meso compound (*RS*; OH groups in a *syn* orientation) and a racemic compound (mixture of *SS* and *RR*; OH groups in an *anti* orientation).^[7] In the following we will name *anti* or *syn*-isomers as the racemate or meso compounds, respectively. Experimentally, **oCB(hmpH)₂** is obtained as a mixture of the *anti*- and the *syn*-diastereoisomers in a 1:0.7 ratio, respectively. Since we have not been able yet to fully separate the *syn*- from the *anti*-forms of **oCB(hmpH)₂**, we have performed the reactions with the *syn/anti* mixture as obtained from the synthesis. In our initial attempts we carried out the reaction of the **oCB(hmpH)₂** with CoCl₂·6H₂O with a ligand to metal ratio of 1:1 in acetone under aerobic conditions. Formation of a complex was evidenced by a rapid color intensification of the solution that became deep violet-blue, this being consistent with an octahedral coordination environment.^[8] After 4–5 days magenta crystals of [CoCl₂(*anti*-**oCB(hmpH)₂**)] were obtained. The molecular structure of the complex determined by X-ray crystallography is depicted in Figure 1. Crystal and data collection details can be found in Table 1 and Experimental Section.

X-ray structure determination of complex [CoCl₂(*anti*-**oCB(hmpH)₂**)] (Figure 1) revealed a distorted octahedral geometry, where each cobalt(II) atom is coordinated by all nitrogen and oxygen atoms of an *anti*-diastereomer of **oCB(hmpH)₂** that is acting as a tetradentate N₂O₂-ligand. Since we employed racemic *anti*-**oCB(hmpH)₂**, crystals for the Co^{II} complex are formed by a racemic mixture of Δ-[CoCl₂(^{RR}*anti*-**oCB(hmpH)₂**)] and Λ-[CoCl₂(^{SS}*anti*-**oCB(hmpH)₂**)] units, which are related by inversion (Figure 1). As in the related Co^{II} complex with the two monosubstituted *o*-carboranyl-

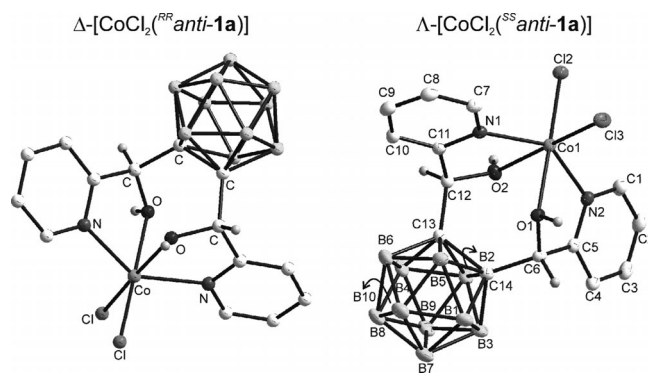


Figure 1. Molecular structure of [CoCl₂(*anti*-**oCB(hmpH)₂**)] thermal ellipsoids set at 35% probability (selected hydrogen atoms are omitted for clarity). Selected interatomic distances /Å and angles /°: Co1–N2 2.124(3), Co1–N1 2.131(3), Co1–O2 2.187(2), Co1–O1 2.199(2), Co1–Cl3 2.3301(9), Co1–Cl2 2.3678(8), N2–Co1–O2 75.60(9), N1–Co1–O2–73.14(9), N2–Co1–O1 74.48(9), N1–Co1–O1 79.52(8), O2–Co1–O1 84.75(8), N1–Co1–Cl3 101.37(7), N2–Co1–Cl2 102.60(8), Cl3–Co1–Cl2 94.05(3).

Table 1. Crystallographic parameters for crystalline structure for complex [CoCl₂(*anti*-**oCB(hmpH)₂**)].

	[CoCl ₂ (<i>anti</i> - oCB(hmpH)₂)]
Empirical formula	C ₁₇ H ₂₈ B ₁₀ Cl ₂ CoN ₂ O ₃
Formula weight	546.50
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions /Å and °	<i>a</i> = 14.3488(4) <i>b</i> = 11.7245(2) <i>c</i> = 16.7150(4) <i>a</i> = 90 <i>β</i> = 107.706(2) <i>γ</i> = 90
Volume /Å ³	2678.80(11)
<i>Z</i>	4
<i>ρ</i> _{calcd.} /g·cm ⁻³	1.355
Absorption coefficient /mm ⁻¹	0.863
<i>F</i> (000)	1116
Crystal	Fragment, violet
Crystal size /mm	0.17 × 0.12 × 0.03
θ range for data collection /°	3.67–28.29
Reflections collected	39036
Independent reflections	6912 [<i>R</i> _{int} = 0.0595]
Completeness to θ /°, %	26.32, 99.64
Max. and min. transmission	0.997 and 0.916
Largest difference peak and hole /e·Å ⁻³	0.67 and –0.50
Data / restraints / parameters	6476 / 2 / 325
Goodness-of-fit on <i>F</i> ²	1.027
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.321
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0873, <i>wR</i> ₂ = 0.1557

alcohol ligands [CoCl₂(**oCB(hmpH)₂**)] (**oCB(hmpH)**, Scheme 1),^[6] the pyridine nitrogens are *trans*-positioned and the oxygen atoms of the chelating ligands and the chloride ions are in a *cis*-position. Selected bond lengths and angles of complex [CoCl₂(*anti*-**oCB(hmpH)₂**)] are given in Figure 1 and are consistent with those of related Co^{II} complexes.^[6] Interestingly, OH group in [CoCl₂(*anti*-**oCB(hmpH)₂**)] remains intact and this leaves the alcohol hydrogen free to act as a proton donor for hydrogen bonding.

The supramolecular structures for these complexes are dominated by non-conventional hydrogen bonds between the chloride anions and the OH moiety of the *o*-carboranylalcohols (Figure 2). The complex forms homochiral ribbons (*RR* or *SS* enantiomeric complexes), along the *b* axis via O–H⋯Cl hydrogen bond interactions (Figure 2). Thus, homochiral recognition seems to be happening in the Co^{II} complexes of **oCB(hmpH)₂**. Each molecule presents both a hydroxyl and chlorine to the adjacent molecule forming a mixed donor/acceptor double interaction along the ribbons (R2,2(8)ring). The distances of all of the observed intermolecular O–H⋯Cl hydrogen bonds are substantially shorter than the 2.95 Å distance that corresponds to the sum of the van der Waals radii (Σ vdW) of hydrogen and chloride atoms (Figure 2) and are near-linear. Thus, they qualify as moderate hydrogen bonds.^[9]

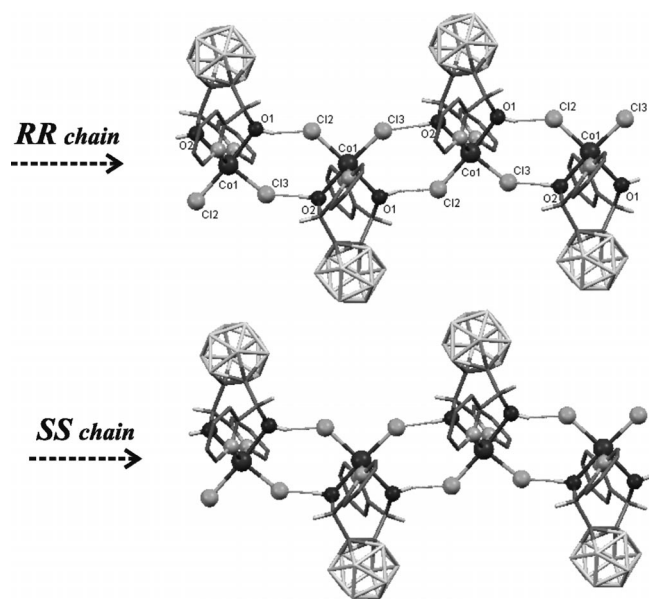


Figure 2. Supramolecular assembly of $[\text{CoCl}_2(\text{anti-}o\text{CB}(\text{hmpH})_2)]$ showing two hydrogen bonded homochiral ribbons (enantiomers indicated with arrows). $[\text{O}(1)\text{--H}\cdots\text{Cl}(2)$ 2.060 Å, $\text{O}(1)\cdots\text{Cl}(2)$ 2.993(2), OHCl 162.08°; $\text{O}(2)\text{--H}\cdots\text{Cl}(3)$ 1.942 Å, $\text{O}(1)\cdots\text{Cl}(2)$ 2.904(2) Å, OHCl 157.78°]. All hydrogen atoms, except those for the CHOH group, are omitted for clarity.

Although the Co^{II} complex is paramagnetic, NMR spectroscopy can be very informative. NMR signals for the **oCB(hmpH)₂** ligand coordinated to the Co^{II} atom were found to be very broad as already observed in the related Co^{II} complex with the monosubstituted ligand $[\text{CoCl}_2(o\text{CBhmpH})_2]$.^[6] Thus, only partial characterization was possible in complex $[\text{CoCl}_2(\text{anti-}o\text{CB}(\text{hmpH})_2)]$. ¹H signals in acetone solutions spanned from 61 to –10 ppm. Regarding the boron atoms from the cluster, they are also affected by the metal and therefore the ¹¹B{¹H} NMR spectrum shows broader resonances than that found for the free ligand. ¹¹B signals spanned from –3 to –32 ppm and are consistent with a *closo*-icosahedral geometry for the boron cages.^[6] Solid state IR spectrum for this complex shows diagnostic signals for the OH and BH stretching frequencies at 3070 and 2576 cm^{–1}, respectively. IR frequencies

for the OH bands are very informative on the presence and strength of hydrogen bonding structures. IR frequency for the OH band in $[\text{CoCl}_2(\text{anti-}o\text{CB}(\text{hmpH})_2)]$ is very broad and red shifted respect to the free ligand (3197 cm^{–1}).^[7] The latter suggests the existence of hydrogen bond interactions between the OH proton and a proton acceptor center present in these molecules, most likely corresponding to the observed O–H⋯Cl hydrogen bonds (Figure 2).

The present results show an unprecedented and distinct tetradentate N₂O₂ type ligand. These novel molecules combine a hydrophobic carborane cluster, two alcohol functionalities and two nitrogenated aromatic rings and represents a new type of C₂-symmetric chiral building block.^[10] Tetradentate ligands, which like ours are not branched, can wrap around an octahedron to afford up to three geometrical isomers (*trans*, *cis-α* and *cis-β*, Figure 3).^[11] Whereas the *trans* isomer is inherently achiral-at metal through the mirror plane, both *cis* isomers have enantiomers with Δ and Λ helicity. Reported tetradentate N₂O₂ ligands are mainly reduced to Schiff base backbone ligands.^[11,12] These ligands and their derivatives coordinate predominantly in a planar arrangement to various metal ions giving *trans* geometries in octahedral complexes. An increased propensity to form *cis* structures have been achieved in some cases by increasing the backbone chain length. Our tetradentate *anti-}oCB(hmpH)₂* ligand, adopts preferentially a *cis-α* configuration around the Co^{II} atom (Figure 1) and it is therefore able to produce chiral-at-metal complexes.

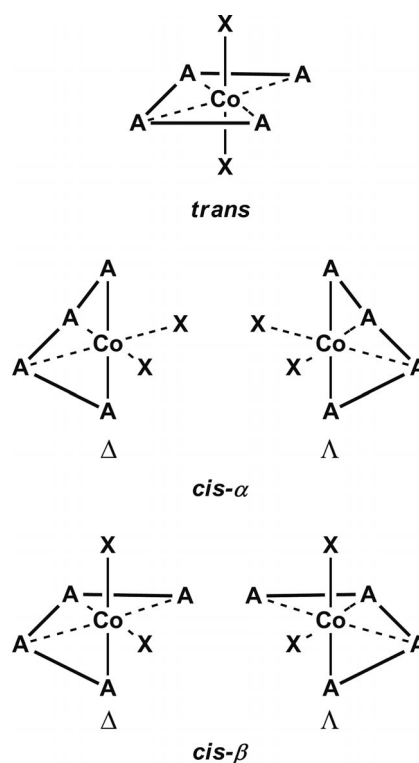


Figure 3. Octahedral-based geometric isomers for not branched tetradentate ligand.

Conclusions

We present here the first metal complex for a new family of the recently reported series of chiral disubstituted *o*-carboranylalcohols (**oCB**(hmpH)₂: (*o*-carboranyl)bis(2-hydroxymethyl)pyridine). X-ray diffraction studies confirmed that *anti*-**oCB**(hmpH)₂ ligand acts as a tetradentate N₂O₂-ligand affording a mononuclear octahedral Co^{II} complex as a racemic mixture of Δ-[CoCl₂(^{RR}*anti*-**oCB**(hmpH)₂)] and Λ-[CoCl₂(^{SS}*anti*-**oCB**(hmpH)₂)]. The supramolecular structure is dominated by non-conventional O–H⋯Cl hydrogen bonds that give rise to homochiral supramolecular ribbons (*RR* or *SS* enantiomeric complexes). The present work also highlights the tendency of this new carborane based tetradentate N₂O₂-ligand to adopt preferentially a *cis-α* configuration around the Co^{II} atom and it is therefore able to produce chiral-at-metal complexes. We are currently working in this direction.

Experimental Section

General Remarks: Reactions were carried out under air. Acetone was used as received. All the other chemicals were commercially available and used as received. IR ATR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer. Elemental analyses were obtained using a CarboErba EA1108 microanalyzer (Universidad Autónoma de Barcelona). **oCB**(hmpH)₂ was prepared as described previously.^[7]

Synthesis and Crystallization of *rac*-[CoCl₂(^{SS}*anti*-**oCB**(hmpH)₂)]

An acetone solution (0.20 mL) of a mixture (0.7/1.0 as obtained from the synthesis) of *syn*- and *anti*-**oCB**(hmpH)₂ (20.0 mg, 0.056 mmol) was added to an acetone solution (0.30 mL) of CoCl₂·6H₂O (13.3 mg, 0.056 mmol) in an open glass vial under air. After the addition of the ligand, the original blue color of the solution turned to deep violet-blue. The vial was then left closed at room temp. and after 4–5 days intense magenta colored crystals were obtained (12.3 mg, 0.022 mmol, 40%). The ¹³C NMR spectrum showed a few very broad and noisy signals that could not be assigned. ¹H NMR (300 MHz): 60.84 (br. s, 2 H, probably H(Py)), 45.66 (br. s, 2 H, probably H(Py)), 28.79 (very brs, 2 H, probably OH), 17.39 (br. s, 2 H, probable OHCH); due to the paramagnetism, unequivocally assignment of the signals was difficult and some aromatic hydrogen atoms were not detected. ¹H ¹B NMR (300 MHz) only BH protons are assigned: –4.75 (s, 2 H), –6.67 (s, 2 H), –8.83 and –10.28 (two overlapped br. s, 4 H), –17.34 (br. s, 2 H). ¹¹B NMR (96 MHz): –3.05 (br. s, 1B), –5 to –15 (m, 4B), –22.33 (br. s, 2B), –31.63 (br. s, 1B). FTIR (ATR): ν_{OH} = 3070; ν_{BH} = 2647, 2569; 1706–650 other signals. Elemental Analysis for C₁₄H₂₂B₁₀Cl₂CoN₂O₂ (M: 632.51 g·mol^{–1}): calculated C 34.44%, H 4.54%, N 5.74%; found C 34.74%, H 4.70%, N 5.39%.

Single Crystal Studies

X-ray reflections for *rac*-[CoCl₂(^{SS}*anti*-**oCB**(hmpH)₂)] were collected at 298 K with an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-*K*_α radiation (λ = 0.7107 Å). Data collection and processing, including a multi-scan absorption correction were performed using CrysAlisPro (version 1.171.33.55),^[13] OLEX2–1.2^[14] and SHELXL97^[15] were used for structure solution and refinement. The OH positions were clear in the difference map and while the O–H

distance was constrained the torsion angles were allowed to refine to coincide with the electron density maxima. The acetone molecule in the latter structure was split over two positions (60, 40) and thermal parameter and geometrical restraints were applied. Those for BH and some CH were placed in idealized positions and refined using a riding model, with C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

CCDC-905024 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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