

Ligand Effects in Low-Valent Co(I) Clathrochelate Complexes

Ophélie Marie Planes,^[a] Rosario Scopelliti,^[a] Farzaneh Fadaei-Tirani,^[a] and Kay Severin^{*[a]}

Abstract: Clathrochelate complexes of cobalt are known in the oxidation states I, II, and III. Low-valent Co(I) complexes are highly reactive compounds, and there is only limited knowledge about their structures in the solid state. Herein, we describe the crystallographic analyses of three low-valent clathrochelate complexes, along with analyses of the corresponding Co(II) precursors. Two different ligand environments were studied: a) ligands with alkyl substituents, which render the complexes highly reducing, and b) potentially redox non-innocent ligands. Our analyses show that the ligands have a large effect on the redox potentials, but only a small effect on the geometry and the electronic state of the central Co ion.

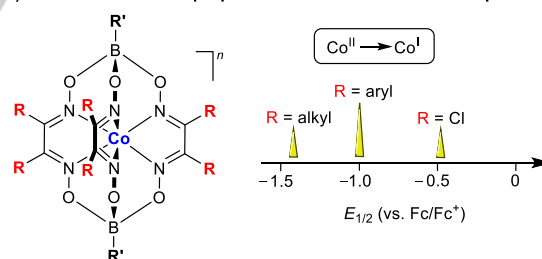
Introduction

In 1968, Boston and Rose described a tris(dimethylglyoximate) Co(III) complex with two B–F capping groups.^[1] The molecular structure of this 'clathrochelate' complex in the solid state was determined two years later, along with the structure of the corresponding Co(II) complex.^[2] Subsequently, Co clathrochelate complexes with boronate ester caps (Figure 1a) were investigated extensively, and numerous structural variations were reported.^[3] Co(II) complexes are formed in reactions of Co salts with dioxime ligands and boronic acids or $\text{BF}_3(\text{OEt}_2)$.^[4] The six lateral groups R can be varied by using an appropriate dioxime, or by post-synthetic modifications.^[5] As apical groups R', aryl-, alkyl- and fluorine substituents have been explored.^[3–5] Co clathrochelate complexes are known in the oxidation states I, II, and III, with most studies focusing on Co(II).^[3–5] These complexes have either a low-spin or a high-spin d^7 electronic configuration, and they display a distorted trigonal prismatic coordination environment.

Co clathrochelate complexes have been employed as catalyst precursors for the electrochemical hydrogen evolution reaction.^[6] In this context, low-valent Co(I) clathrochelates are of special interest, because they could be involved in the formation of the catalytically active species. A first crystallographic analysis of a Co(I) clathrochelate was reported by Voloshin and co-workers in 2005.^[7] In order to stabilize the highly reactive reduced form, they have used a complex with six chloro substituents R in lateral

position. Due to the electron-withdrawing nature of the chloride substituents, it is possible to achieve the reduction of the Co(II) precursor at rather high potential ($E_{1/2} = -0.46$ V for R = Cl and R' = Bu; ref. = Fc/Fc⁺ Figure 1a).^[8] In the meantime, the solid state structures of two other Co(I) clathrochelates have been reported: one complex with R = Cl and R' = Ph ($E_{1/2} = -0.50$ V),^[8] and another complex with R = Ph and R' = dithiophenyl ($E_{1/2} = -1.03$ V).^[9,10] Complexes with alkyl groups in lateral position display a more negative reduction potential ($E_{1/2} \sim -1.4$ V), impeding isolation and structural characterization. A theoretical analysis of a Co(I) clathrochelate with R = Me came to the conclusion that the complex should feature a high spin Co(I) center ($S = 1$) in a highly symmetric ligand environment.^[11] However, the possibility that Co(I) clathrochelate complexes could adopt a singlet spin state ($S = 0$) was also considered in theoretical studies.^[11,12] The calculations indicate that a diamagnetic Co(I) complex would show a very distorted ligand environment, with two long Co–N bonds. Below, we report the first structural characterization of Co(I) clathrochelate complexes with alkyl groups in lateral position. Furthermore, we have prepared a Co(II) clathrochelate with a potentially redox non-innocent phenanthrenequinone imine ligand (Figure 1b),^[13] and we have examined the influence of this ligand on the structure of the corresponding low-valent Co(I) complex.

a) Structure and redox properties of Co clathrochelate complexes



b) Phenanthrenequinoneimines as redox non-innocent ligands

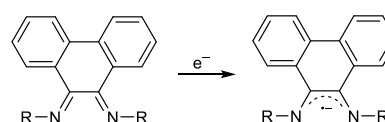


Figure 1. a) General structure of Co clathrochelate complexes with boronate ester caps, and typical redox potentials of the Co(II)/Co(I) transition for different lateral groups R. b) Phenanthrenequinoneimines can act as redox non-innocent ligands. Their incorporation in Co clathrochelate complexes is explored herein.

Results and Discussion

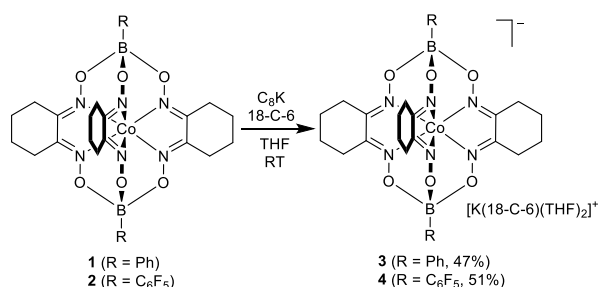
For our investigations, we have prepared the known complex **1** from CoCl_2 , nioxime, and phenylboronic acid using an adapted literature procedure (Scheme 1).^[4d-e] The new complex **2** with

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terminal B-C₆F₅ groups was prepared in an analogous fashion in 53% yield. Both complexes were characterized by high resolution mass spectrometry, elemental analysis, UV-Vis spectroscopy, cyclic voltammetry, and single crystal X-ray analysis (for details, see the Supporting Information, SI). The presence of electron-withdrawing pentafluorophenyl groups in **2** was found to have a negligible influence on the reduction potential: the reversible Co(II)/Co(I) transition of **1** occurs at $E_{1/2} = -1.40$ V, and the corresponding wave for **2** is found at $E_{1/2} = -1.42$ V (CH₂Cl₂, 0.1 M TBAPF₆, ref. = Fc/Fc⁺).



Scheme 1. Synthesis of the low-valent complexes **3** and **4** by reduction of the Co(II) clathrochelates **1** and **2** with C₆K (1.2 equiv) in the presence of 18-crown-6 (18-C-6, 1.2 equiv).

clathrochelates.^[3–5,8] For an ideal trigonal prismatic coordination environment, the Bailar twist angle φ is 0°, whereas an octahedral complex has a twist angle of $\varphi = 60^\circ$. For **1** and **2**, we observe small twist angles of 4.9° and 1.7°, respectively (Table 1).

The reduction of the Co(II) complexes **1** and **2** was achieved by using C₆K and 18-crown-6 in THF at room temperature. Within 30 min, dark blue solutions were obtained, from which we were able to obtain the low-valent complexes **3** and **4** in 47% and 51% yield, respectively. Single crystals were obtained by slow diffusion of pentane into solutions of **3** and **4** in THF. Crystallographic analyses were performed for both products, and graphic representations of the solid state structures are depicted in Figure 2.

The average Co–N bond distances of **3** (1.992 Å) and **4** (1.991 Å) are very similar to what was found for **1** (1.970 Å) and **2** (1.968 Å). However, we do not observe a pronounced bond lengths alternation. Instead, all six Co–N bond are nearly equidistant (Table 1). The highly symmetric ligand environment points to the presence of high spin Co(I) centers.^[7–9,11] The geometry around the Co ions is nearly perfectly trigonal prismatic, with small twist angles φ , and B...Co...B' angles of close to 180°. Overall, the structural data of **3** and **4** are very similar to what has been observed for the three other Co(I) clathrochelate complexes reported in the literature. It can be concluded that the electronic character of the dioximato ligand does have a pronounced effect on the redox potential of the Co(II)/Co(I) transition (Figure 1a), but not on the electronic situation of the reduced Co center.

Table 1. Selected bond lengths [Å] and angles [°] for the complexes 1–6.

complex	1	2	3	4	5	6
Co1–N1	1.9058(14)	1.8986(8)	2.0004(19)	1.991(7)	2.160(5)	2.011(3)
Co1–N2	2.1023(13)	2.1183(9)	1.9840(20)	1.981(7)	1.902(5)	2.000(3)
Co1–N3	1.8928(13)	1.8865(8)	1.9978(17)	2.009(7)	1.896(5)	2.021(2)
Co1–N4	1.8886(13)	1.8913(9)	1.9807(17)	1.994(7)	2.127(5)	2.018(2)
Co1–N5	2.1254(15)	2.1135(9)	2.0072(19)	1.972(7)	1.907(5)	2.012(2)
Co1–N6	1.9022(14)	1.9001(8)	1.9817(19)	1.998(7)	1.915(5)	1.994(3)
Co–N _{av.}	1.970	1.968	1.992	1.991	1.985	2.009
NC–CN _{av.}	1.455	1.454	1.457	1.447	1.466	1.467
φ (NBB'N')	4.9	1.7	1.5	0.88	0.44	0.88
ϕ (BCoB')	173	172	180	179	172	179

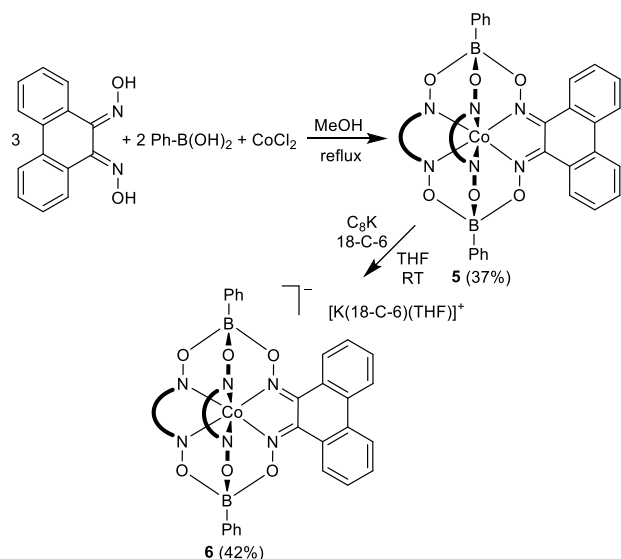
Figure 2. Molecular structures of the complexes **1–4** in the crystal. Hydrogen atoms are not shown for clarity. The thermal ellipsoids are at 50% probability.

The molecular structures of **1** and **2** in the crystal show an approximate trigonal prismatic coordination geometry around the Co ions (Figure 1). Due to Jahn-Teller distortion, one can observe four short Co–N bond distances of ~ 1.89 Å, and two long Co–N bond distances of ~ 2.11 Å (Table 1). The presence of short and long Co–N bonds is a characteristic feature of low-spin Co(II)

Next, we have investigated Co clathrochelate complexes with phenanthrenequinone dioximato ligands, which are potentially redox non-innocent.^[13] The Co(II) complex **5** was prepared in 37% yield from CoCl₂, phenanthrenequinone dioxime,^[14,15] and phenylboronic acid. Complex **5** shows good solubility in CH₂Cl₂ and HF. The solid could be exposed to air without any noticeable decomposition.

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The molecular structure of **5** was determined by single crystal X-ray diffraction, and a graphic representation of the structure is depicted in Figure 3. As observed for **1** and **2**, the encapsulated Co ion shows a distorted trigonal prismatic ligand environment, with two longer and four shorter Co–N bonds (Table 1). With 1.985 Å, the average Co–N bond distance is slightly larger than what was found for **1** and **2** (1.970 Å and 1.968 Å).



Scheme 2. Synthesis of the clathrochelate complexes **5** and **6**.

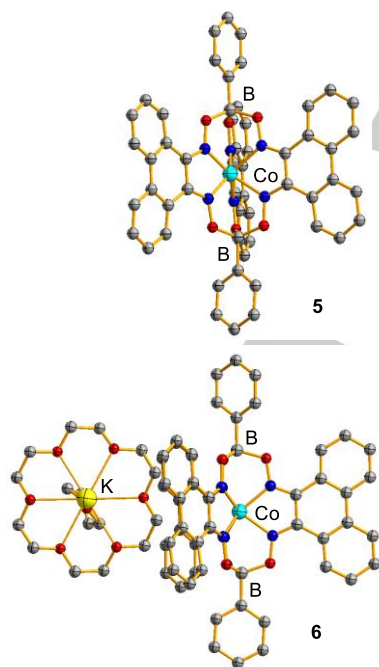


Figure 3. Molecular structures of the complexes **5** and **6** in the crystal. Hydrogen atoms are not shown for clarity. The thermal ellipsoids are at 50% probability.

The redox behavior of **5** was examined by cyclic voltammetry (CH_2Cl_2 , 0.1 M TBAPF₆, ref. = Fc/Fc⁺). Two reversible transitions

were observed at $E_{1/2} = -0.10$ V and $E_{1/2} = -0.85$ V. The former transition is assigned to the Co(II)/Co(III) redox couple. The transition at -0.85 V could be related to either a ligand- or a metal-based reduction of the neutral Co(II) complex **5**.

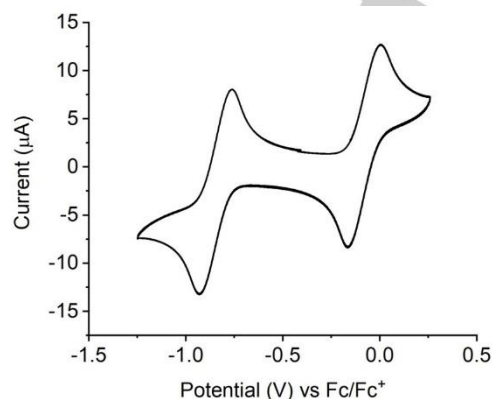


Figure 4. Cyclic voltammogram of complex **5** in DCM with TBAPF₆ (0.1 M) as electrolyte. (CE and WE: Pt, RE: 3M NaCl). Scan rate = 100 mV.s⁻¹.

To elucidate the nature of the reduced state, we have carried out a reaction of complex **5** with C₈K in THF in the presence of 18-crown-6 (Scheme 2). Stirring for 2 h at room temperature resulted in the formation of a green solution. Complex **6** could then be isolated in 42% yield by precipitation with diethyl ether. Single crystals of **6** were obtained by slow evaporation of a THF solution of **6** in a glovebox, and a crystallographic analysis was performed (Figure 3).

The coordination environment of the Co ion in complex **6** is very similar to what was found for **3** and **4**: one can observe six nearly equidistant Co–N bonds, and only a small distortion from an ideal trigonal prismatic coordination environment (Table 1). If complexes with phenanthrenequinone imine ligands undergo a ligand-based reduction, one can typically observe a shortening of the NC–CN bonds (~ 0.07 Å).^[13] For complex **6**, however, the corresponding values are very similar to those of **5**. Taken together, the structural data are good evidence that clathrochelate **6** should be described as a Co(I) complex.

Conclusions

Following the discovery that Co clathrochelate complexes can be employed as catalyst precursors for the hydrogen evolution reaction, low-valent Co(I) clathrochelates have been studied extensively, both from an experimental as well as theoretical point of view.^[7–12] Despite these efforts, there was only limited knowledge about the solid state structure of these highly reactive complexes. We have performed crystallographic analyses of three low-valent clathrochelate complexes (**3**, **4**, and **6**), along with analyses of the corresponding Co(II) precursors. The nioxime-derived complexes **3** and **4** have alkyl substituents in lateral position, and they are significantly more reducing than the Co(I) complexes with phenyl and chloro substituents described in the literature.^[7–9] Complex **6**, on the other hand, features phenanthrenequinone dioximato ligands, which are potentially redox non-innocent. Our analyses show that the ligands have a

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large effect on the redox potentials, but only a small effect on the geometry and the electronic state of the central Co ion. The three low-valent complexes described herein are all Co(I) complexes with a nearly ideal trigonal prismatic coordination environment.

Experimental Section

Experimental details and analytical data are given in the Supporting Information.

X-Ray crystallography: CCDC codes for complex

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Keywords: cobalt • coordination chemistry • clathrochelate complex • electrochemistry • X-ray crystallography

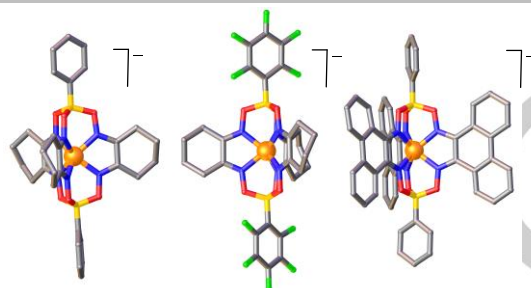
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FULL PAPER

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Clathrochelate Complexes of Co(I)

Coordination chemistry

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