

New antimony-capped iron(II) and cobalt(III) clathrochelate precursors of the polytopic hybrid cage complexes: Synthesis, X-ray structures and electrochemistry

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Abstract

Direct template macrocyclization of the three dimethylglyoxime molecules on the iron(II) ion and the capping of nonmacrocylic K_3CoDm_3 tris-dimethylglyoximate with triethylantimony(V) derivatives led to the formation of triethylantimony-capped iron(II) and cobalt(III) clathrochelates. The complexes obtained have been characterized using elemental analysis, MALDI-TOF mass, IR, UV–Vis, ^{57}Fe Mössbauer and 1H and ^{13}C NMR spectroscopies, and X-ray crystallography. The influence of the nature of an encapsulated metal ion, the capping groups and the chelate fragments on a clathrochelate framework geometry is discussed. The cyclic voltammograms show oxidation and reduction waves assignable to $Fe^{2+/3+}$ and $Co^{2+/3+}$ couples of the encapsulated metal ion.

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1. Introduction

Polytopic d-metals cage complexes with relatively spatially and electronically independent fragments that are linked by a system of σ - and π -bonds, have been proposed as promising entities for the design of molecular (photo)electronic devices and mechanical molecular machines [1,2].

The synthesis of such complexes by a direct template reaction is hindered or not possible in principle. The polytopic hybrid iron(II) α -oximehydrazonates and α -dioximates have been obtained by transmetallation reactions of the initially synthesized labile antimony-capped precursors [1–3] (Fig. 1). However, the presence of only one reactive macrobicyclic precursor of apically functionalized hybrid

tris-dioximate clathrochelates, the triethylantimony-capped $FeNx_3(Sb(C_2H_5)_3)_2$ complex (where Nx^{2-} is cyclohexandione-1,2-dioxime (nioxime) dianion), limits the possibilities for obtaining such hybrid polytopic compounds. Moreover, the cobalt complexes of this type, which are most promising for the development of mentioned above devices and machines because of the formation of stable species with an encapsulated metal ion in different oxidation states (usually, the encapsulated cobalt(II) and cobalt(III) ions), have not been synthesized previously.

Therefore, we attempted to synthesize the di(triethylantimony)-capped iron(II) and cobalt(III) clathrochelates, which are derivatives of the available dimethylglyoxime, as potential precursors of polytopic iron(II) and cobalt-(II,III) cage compounds. Using the X-ray crystallography data obtained, we also discuss the influence of the nature of an encapsulated metal ion, the capping groups and the chelate fragments on a clathrochelate framework geometry.

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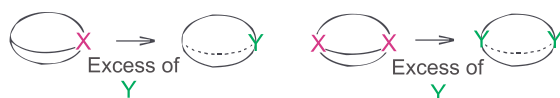


Fig. 1. Exchange of capping group(s) (transmetallation) reaction.

2. Experimental

2.1. General procedures

The reagents used, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dimethylglyoxime (H_2Dm), sorbents, organic bases, and solvents were obtained commercially (Fluka). K_3CoDm_3 complex was prepared as described elsewhere [4]. The triethylantimony(V) dibromide was synthesized by known procedure [5]. The triethylantimony(V) carbonate was obtained from triethylantimony(V) dibromide with Na_2CO_3 in methanol.

The analytical, IR, UV–Vis, NMR, ^{57}Fe Mossbauer and electrochemicals data were obtained as described previously [2] (see Supplementary material for the experimental details, IR and NMR data).

2.2. Syntheses

2.2.1. $\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2$

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.20 g, 1 mmol), dimethylglyoxime (0.38 g, 3.3 mmol) and NaClO_4 (1.5 g) were dissolved/suspended in methanol (15 ml) under argon. The reaction mixture was stirred at 50°C for 1.5 h and the solution of $(\text{C}_2\text{H}_5)_3\text{SbCO}_3$ (0.59 g, 2.2 mmol) in methanol (5 ml) was added. After stirring for 10 min, the reaction mixture was added dropwise to the stirring suspension of CaCO_3 (2 g) in 10% aqueous methanol (30 ml). The solution/suspension obtained was stirred for 30 min and then filtered. The precipitate was washed with methanol and dissolved in methylene dichloride. The methylene dichloride extract was filtered, evaporated to a small volume (~ 1.5 ml) and precipitated with hexane. The solid product was filtered, washed with hexane and dried *in vacuo*. Yield: 0.36 g (40%). *Anal. Calc.* for $\text{C}_{24}\text{H}_{48}\text{N}_6\text{O}_6\text{FeSb}_2$: C, 35.32; H, 5.94; N, 10.30; Fe, 6.84. *Found*: C, 35.20; H, 6.00; N, 10.31; Fe, 6.98%. *MS* (MALDI-TOF): m/z (I , %): 845(100) $[\text{M} + \text{Et}]^+$, 816(20) $[\text{M}]^+$, 729(70) $[\text{M} - 3\text{Et}]^+$. *UV–Vis* (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^{-3}$, $\text{mol}^{-1} \text{l cm}^{-1}$) 270 (6.5), 300 (13), 330 (2.5), 355 (0.6), 389 (0.8), 424 (0.6), 450 (2.1), 476 (3.3), 536 (3.0).

2.2.2. $[\text{CoDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2]\text{Br}$

Complex K_3CoDm_3 (1 g, 1.9 mmol) and $(\text{C}_2\text{H}_5)_3\text{SbBr}_2$ (1.55 g, 4.2 mmol) were dissolved in methanol (25 ml), the reaction mixture was stirred for 1 h and then rotary evaporated to dryness. The solid residue was washed with diethyl ether (20 ml) and filtered. The precipitate was washed with diethyl ether (30 ml, in 3 portions), and dissolved in methylene dichloride. The methylene dichloride solution was filtered and precipitated with hexane. The precipitate was

washed with diethyl ether, reprecipitate from chloroform with hexane, washed with hexane and dried *in vacuo*. Yield: 0.90 g (50%). *Anal. Calc.* for $\text{C}_{24}\text{H}_{48}\text{N}_6\text{O}_6\text{BrCoSb}_2$: C, 32.06; H, 5.39; N, 9.35. *Found*: C, 32.22; H, 5.32; N, 9.41%. *MS* (MALDI-TOF): m/z 819 $[\text{M} - \text{Br}]^+$. *UV–Vis* (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^{-3}$, $\text{mol}^{-1} \text{l cm}^{-1}$) 256 (28), 278 (9.0), 299 (8.5), 337 (6.3), 382 (1.4), 408 (1.0).

2.3. X-ray crystallography

The details of crystal data collection and refinement parameters for $\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2$ and $[\text{CoDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2]\text{Br} \cdot 2.5\text{CHCl}_3$ complexes are listed in Table 1. Single crystals of these complexes were grown from methylene dichloride – hexane and chloroform – heptane mixtures, respectively.

Data were collected with a Bruker SMART 1K CCD diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, ω -scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 60^\circ$) at 295 K $\{\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2\}$ and 120 K $\{[\text{CoDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2]\text{Br} \cdot 2.5\text{CHCl}_3\}$. Reflections intensities were integrated using SAINT software [6] and corrected for absorption by semi-empirical method using SADABS program [7].

Due to the proximity of all angles to 90° in the $\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2$ unit cell, the choice of crystal system was done on the base of the detail analysis of the R_{int} values and systematic absences for all possible variants. All attempts to describe the crystal as a twin (monoclinic which emulate orthorhombic) gave no any change in the convergence factors as well as the standard deviations and residual Fourier electron density synthesis.

The structures were solved by the direct method and refined by full-matrix least squares method against F^2 of all data using SHELXTL-97 [8]. Non-hydrogen atoms were refined in anisotropic approximation (except for methyl groups in the $\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2$ molecules). Positions of hydrogen atoms were calculated and included in refinement in isotropic approximation by the riding model with $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{C})$, where $n = 1.5$ for methyl groups and 1.2 for the other groups.

The terminal methyl groups in $\text{FeDm}_3(\text{Sb}(\text{C}_2\text{H}_5)_3)_2$ molecule are disordered at two positions with occupation 3:2 (C14 and C14' atoms), 4:1 (C16 and C16' atoms, C22 and C22' atoms), 1:1 (C18 and C18', C20 and C20', C24 and C24' atoms), and were included in refinement in isotropic approximation with constrained C–C bond lengths (1.50 Å). One of the chlorine atoms of one of the solvate chloroform molecules is disordered at two positions (C19 and C19') with occupation 7:3.

3. Results and discussion

3.1. Synthesis

The synthesis of the labile in transmetallation reactions antimony-capped clathrochelates is a key step in the prep-

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