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Syntheses of the $B_{(8)}$-hydroxy- and $B_{(8,8')}$-dihydroxy-derivatives of the bis(1,2-dicarbollido)-3-cobalt(1-)ate ion by its reductive acetoxylation and hydroxylation: molecular structure of $[8,8'\text{-}\mu\text{-}CH_3C(O)_2<(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^0$ zwitterion determined by X-ray diffraction analysis

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Abstract

Preparative routes to 8-hydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**2**) and 8,8′-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**3**) ions are reported by the reductive acetoxylation of the parent bis(dicarbollido)cobaltate ion (**1**) followed by hydrolysis of the intermediates. The essential reagent is acetic anhydride, and strong acids are required as catalysts. For the hydroxyderivative ion **2** the simultaneous presence of acetic acid brings benefit, whereas it is detrimental for the formation of the dihydroxyderivative **3**. Reaction intermediate leading to the dihydroxy derivative is the already reported $[8,8'\text{-}\mu\text{-}CH_3C(O)_2<(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^0$ zwitterion. This compound was adequately characterised for the first time and its molecular structure as determined by X-ray diffraction analysis is presented. Both B-hydroxylated bis(dicarbollido)-ions can be alternatively obtained on the direct hydroxylation of the parent ion by hot 60–80% sulphuric acid. Optimised synthetic procedures and the main physicochemical properties (MS, TLC, HPLC, ^{1}H- and ^{11}B-NMR) of the species are presented. The probable reaction course of the reductive acetoxylation is discussed.

Keywords: Bis(1,2-dicarbollido)-3-cobalt(1-)ate ion; Carbaboranes; Metallacarboranes; Reductive acetoxylation; Hydroxy and dihydroxy derivatives; X-ray crystallography

1. Introduction

The chemistry of the [*closo-commo*-$(1,2\text{-}C_2B_{10}H_{11})_2$-3-Co]$^-$, bis(1,2-dicarbollido)-3-cobalt(1-)ate ion [1,2] (**1**) has been continuously developed over nearly four decades. It has been reviewed several times, most recently and comprehensively in 1999 [3]. From the synthetic chemistry point of view, the main characteristic feature of **1** is the ability of this ion to undergo an easy substitution of its $B_{(8,8')}$-terminal hydrogens, under acid catalysis, for a variety of nucleophiles, L. This leads to the formation of the respective $B_{(8)}$–L and $B_{(8,8')}$–L_2 derivatives (or bridged structures). Many examples are reported in the above-mentioned review [3] and in citations therein. Such reactions are virtually unknown to organic chemistry but are frequent with a plethora of deltahedral boron cluster compounds. We have suggested to their designation as Electrophile Induced Nucleophilic Substitutions (EINS) [4]. Basic principles of such reactions are as follows: an electrophile, eventually generated in situ, abstracts the most hydridic terminal hydrogen from the most negative B–H vertex of the boron cluster and the transient vacant B-orbital then becomes attacked by the most nucleophilic or most abundant moiety from the environment. In **1,** the most negative vertices are $B_{(8)}$–H and the symmetry equivalent $B_{(8')}$–H position.

Our group has been involved in substitution chemistry of **1** from the very beginning, especially aimed at

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the development of synthetic routes to derivatives of **1** as advanced extraction agents for recovery of radionuclides from nuclear waste [5]. Recently, a new target in this area was set up, i.e. synthesis of derivatives of **1** bearing functional groups containing donor atoms like O, N, P [6]. Such groups would accomplish tight bonding and would allow for transfer into organic phase in the liquid–liquid extraction process even for polyvalent cations such as lanthanides and actinides [7]. To meet these requirements, we have performed a search for reactions which might modify the parent ion **1** by introduction of simple reactive substituents at the most reactive vertices. These groups have been expected to serve as effective derivatisation sites enabling binding of a variety of functionalities to the **1** framework via a $B_{(8)}$–E connection. In this respect, the 8-hydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**2**) and the 8,8′-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**3**) ions seemed particularly attractive. Compound **2** has not been reported in the literature, yet. Anion **3** was described as resulting upon solvolysis of the bridged zwitterion $[8,8'\text{-}\mu\text{-}CH_3CH(O)_2<(1,2\text{-}C_2B_8H_{10})_2\text{-}3\text{-}Co]^0$ (**4**). This species was obtained in low yield on treatment of **1** with acetic acid and some acetic anhydride with catalysis of perchloric acid [8]. Characterisation of **3** in this original paper was rather poor and the suggested mechanism of formation of **4** was certainly incorrect because a direct reaction of **1** with acetic acid was presumed, and acetic anhydride was designated to serve only for continuous removal of the liberated water. However, this brief report in the literature indicated a possible potential of 'reductive acetoxylation' of **1** for eventual preparative procedures leading to **2** and **3** on a larger scale, and thus promoted our deeper study presented in this article. Alternatively, even simpler novel methods for synthesis of compounds **2** and **3** in preparative scale are described here. This consists in direct hydroxylation of anion **1** with diluted sulphuric acid.

2. Experimental

2.1. General

Cesium bis(1,2-dicarbollido)-3-cobalt(1-)ate (**1**) was supplied by Katchem Ltd, Prague. Ac_2O, AcOH, sulphuric acid and all solvents were commercial analytical grade reagents; and used without further treatment. All reactions were carried out under ambient atmosphere. For column chromatography silica gel Aldrich 200–400 mesh was used. TLC vas performed on Silufol (silica gel on aluminium foil, 5% starch as the binder); orange or yellow spots were amplified by diiodine vapour. Melting points were measured in sealed capillaries and are uncorrected. Analyses were performed in the I.I.C. Analytical Department using standard procedures. The NMR spectra were measured in deuterioacetone in a Varian Unity 500 spectrometer at 500 MHz for ^1H and at 160.4 MHz for ^{11}B-NMR. The procedures for [^{11}B–^{11}B]-COSY 2D NMR [9,10] and for ^1H-{^{11}B}selective decoupling [11] were exploited as in our other previous papers [12]. Mass spectra of the uncharged species were measured on a Magnum GS-MS ion trap system (Finnigan MAT, USA) equipped with heated inlet option (Spectronex AG., Basel). High resolution mass spectra of ionic species were measured on Esquire 3000 Ion Trap System, and alternatively re-measured in Bruker Esquire-LC Ion Trap instrument using Electrospray Ionisation. Negative ions were detected. Samples dissolved in MeCN (concentrations 1 ng μl^{-1}) were introduced to ion source by infusion of 3 $\mu l\,min^{-1}$, drying temperature was 300 °C, drying gas flow 5 l/min, nebulising gas pressure 10 psi. Single crystal X-ray diffractions were measured in a Nonius KappaCCD device (see below).

2.2. Analytical HPLC

Equipment: Analytical system Merck-Hitachi, 6200 Intelligent pump, D-6000 interface, Rheodyne 7125 injection valve with 20 μ sample loop, 7400 Diode Array detector with 7000 Manager Software. *Chromatographic procedure:* The Ion-Pair RP chromatographic method for separation of hydrophobic borate anions [13] with DAD was used with modification described earlier in literature [14] by the authors of this Group. *Column:* RP Separon C8 7 μ (silica with chemically bonded octyl groups) Tessek, Prague. *Mobile phase:* 3 mmol hexyl amine acetate in 58% aqueous MeCN, pH adjusted to 5.5 by AcOH, flow rate 1 ml/min, detection DAD, fixed wavelengths 290, 302, 308 and 325 nm; sensitivity range 0.2 A.U.F.S.; sample concentrations ca. 1 mg/ml, injected volume 5 μl. Respective values of capacity factors k' for studied compounds **2**, **3** and **4** were 1.73, 1.05 and 4.53, respectively, compound **4** being always partly hydrolysed to **3** upon treatment with aqueous mobile phase, therefore the samples from orientation experiments were hydrolysed before the analyses, and the content of the respective compounds **2** and **3** was determined. Parent anion exhibited capacity factor $k' = 3.71$ under these conditions. The method was used also for purity check of anions **2** and **3**.

2.3. Orientation experiments

All experiments were carried out with **1**-Cs salt (0.5 g, 1.1 mmol), alternatively in AcOH or Ac_2O or in a mixture of both reactants; total volume was 3 ml in every case. In the acid catalysed experiments conc. H_2SO_4 (0.1 ml, 1.84 mmol) was added. The mixtures were heated to 80 °C for 2 h and monitored by TLC. Where no TLC change was observed till the end of the

experiment, it was considered as *no reaction*. This was the case of all experiments without sulphuric acid and in AcOH + sulphuric acid but without Ac_2O. In other cases the reactions were stopped by addition of enough water to decompose the initial amount of Ac_2O, then the mixtures were heated to 80 °C for an additional 1 h to hydrolyse all intermediates, by a slow addition of 25% water solution of NH_3 (0.5 ml). The strong acids were neutralised and the mixture was evaporated in vacuum to dryness. The content of **1**–**3** and minor by-product was assessed by HPLC.

Series a—no reaction. With AcOH without Ac_2O; with/or without sulphuric acid; with Ac_2O but without sulphuric acid.

Series b—successful reductive acetoxylations. The components:**1** + AcOH + Ac_2O + sulphuric acid in molar ratios 1:45:3:1.7 afforded **2** (72%) and recovered **1** (10%); the rest were eight minor side products with HPLC k' value under 1.0. The components **1** + Ac_2O + sulphuric acid in molar ratios 1:30:1.7 gave **3** (60%) and **2** (11%) and about 30% of a mixture of eight minor side products; no **1** was found in this case.

2.4. Synthesis of **2**

2.4.1. Via reductive acetoxylation of **1**

In a solution of H_2SO_4 (2.2 ml, 40 mmol) in AcOH (20 ml, 333 mmol) **1**-Cs salt (9.2 g, 20 mmol) was dissolved, Ac_2O (8 ml, 80 mmol) was added and the mixture was heated to 80 °C for 5 h; after cooling down the separated $CsHSO_4$ was filtered, washed twice with AcOH (5 ml) and set aside for the final precipitation of the crude product. To the combined filtrates water was added (30 ml), a small amount of solids was filtered off (0.65 g of a mixture of **4** + **5** in ratio ca. 8:1 according to TLC) and the volatiles were stripped off in vacuo to leave a viscous residue; this was dissolved in water (100 ml) and heated to 80 °C for 1 h. The above-mentioned crude $CsHSO_4$ was dissolved in water (20 ml), the solution was filtered to the former hot solvolysate, the mixture was made slightly alkaline by addition of about 2 ml of 25% solution of NH_3 in water and left to cool overnight. The fluffy mixture of separated Cs-salts was filtered off, rinsed twice with water (10 ml), dried in vacuum, dissolved in 30 ml of a mixture of MeCN–$CHCl_3$ (1:2 v/v), soaked into a column of silica gel (i.d. 2 cm, length 20 cm) and chromatographed with the same solvent mixture. The first band (TLC $R_F = 0.30$) contained recovered **1**-Cs salt (0.83 g, 9%), the main band (TLC $R_F = 0.18$) of the **2**-Cs salt followed next (6.03 g, 63.6%). A mixture of more hydroxylated side product remained near the start and was not further considered. If accounting the recovered **1**-Cs salt, the yield of **2**-Cs was 70%.

2.4.2. Direct hydroxylation of **1**

A stirred suspension of **1**-Cs (2.0 g, 4.4 mmol) in 60% aqueous sulphuric acid (450 ml) was heated to 120 °C (bath temperature); small samples were withdrawn in 30 min intervals and analysed by HPLC. After 4.5 h the starting **1** disappeared and the product contained only **2** (82%) and **3** (18%). The mixture was diluted with water (200 ml) and the conjugate acids were extracted twice with Et_2O (30 ml). To the combined extracts water (30 ml) was added, ether was stripped off in vacuum along with ca. 15 ml of water and 1.0 M CsOH (6 ml) was added to precipitate mixed Cs-salts. The precipitate was filtered, recrystallised from hot 60% EtOH (ca. 20 ml); the separated crystals contained still 9% of **3**-Cs salt. After drying in vacuum all was dissolved in MeCN (10 ml), the filtered solution was diluted with $CHCl_3$ (20 ml) and left overnight. Nearly pure crystals of **3**-Cs salt were filtered off and the mother liquors were evaporated in vacuum to give almost pure (> 97% purity by HPLC assay) **2**-Cs salt; 1.27 g (61%).

2.5. General properties of the **2**-salts

All salts with **2** are by far more soluble than analogous **1**-salts in all solvents, and are less prone to give well developed crystals. In general, **2**-salts are insoluble in dry Et_2O, $CHCl_3$, CH_2Cl_2 and water. They dissolve well in acetone, MeCN, in a mixture of MeCN–$CHCl_3$ (1:2 v/v) and in dilute EtOH. Their TLC R_F values depend on the counterion because a tight ion pair is apparently moving at the TLC sheet, for instance: $R_{F\text{-}Cs} = 0.18$, $R_{F\text{-}HNMe3} = 0.30$, $R_{F\text{-}HNEt3} = 0.39$. These values are on average just 45% of those of analogous **1**-salts.

Trimethyl ammonium 8-hydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate **2**-$HNMe_3$ salt: m.p.: > 300 °C, $m/z = 343$, corresponding to the $[^{11}B_{18}^{12}C_4^1H_{22}^{16}O^{59}Co]^-$ ion, m/z_{max} (100%) = 340.1. Anal. Calc. for $B_{18}C_7H_{32}ONCo$:B 48.67%, found 48.23%. HPLC k' value = 1.73; ^{1}H-NMR (in deuterioacetone): 3.95 ppm (s, 2H, $CH_{carbor.}$); 3.85 ppm (s, 2H, $CH_{carbor.}$); 6.44 ppm (broad s, 1H, HN^+); 3.01 ppm (s, 9 H, $(CH_3)_3N^+$). ^{11}B-NMR: ppm ($J_{(B-H)}$) [^{1}H-{^{11}B}], selectively decoupled]($B_{(assign.)}$):26.44 (s) (B_8); 6.84 (134) [3.098] ($B_{(8')}$); − 0.26 (139) [2.825] ($B_{(10')}$); − 3.79 (143) [2.566] ($B_{(10)}$); − 5.18 (142) [2.645] ($B_{(4',7')}$); − 5.66 (157) [2.107] ($B_{(9,12)}$); − 6.72 (146) [1.884] ($B_{(9',12')}$); − 8.73 (154) [2.806] ($B_{(4,7)}$); − 17.49 (150) [1.580] ($B_{(5',11')}$); − 19.41 (170) [1.545] ($B_{(5,11)}$); − 22.36 (167) [1.689] ($B_{(6')}$); − 30.07 (165) [1.340] ($B_{(6)}$).

2.6. Synthesis of the zwitterion **4**

2.6.1. From **1**-Cs salt

In a solution of sulphuric acid (4.4 ml, 80 mmol) in AcOH (50 ml, 820 mmol) and Ac_2O (20 ml, 200 mmol),

1-Cs salt (18.4 g, 40 mmol) was dissolved with occasional shaking and the mixture was left overnight. The separated white crystals of $CsHSO_4$ were filtered off, rinsed twice with Ac_2O (5 ml). The mother liquors were combined with the washings and heated to 80 °C for 5 h. AcOH was stripped off in vacuum, the dark orange oily residue was diluted with Ac_2O (20 ml) and heated to 80 °C for additional 2 h. A large amount of a dark orange solid separated during this period. After cooling down, water (10 ml) was added in small portions with external cooling with tap water in order to hydrolyse residual Ac_2O. The slurry was vacuum filtered, the solid rinsed twice with 80% AcOH (10 ml) and then dried in vacuum (150 Pa, 40 °C) to a constant weight. It was extracted ten times with CH_2Cl_2 (50 ml) in a vacuum extractor; the product gradually accumulated in the extraction flask. It was filtered off by suction and dried in vacuum; 8.2 g of this first crop of **4** was obtained. The mother liquors were carefully covered with hexane (100 ml) and left undisturbed for 3 days. Dark orange prisms (X-ray quality) of **4** were obtained; 1.26 g. Total yield was 62.0%. Evaporation of the red mother liquors after this second crop of **4**, and subsequent column chromatography at silica gel (i.d. 10 mm, length 150 mm) furnished **5**, 0.12 g (0.8%), identified by m/z_{max} 386 and by comparative TLC with an authentic sample.

*2.6.2. From **2**-Cs salt*

To a solution of **2**-Cs salt (1.0 g, 2.1 mmol) in Ac_2O (5 ml, 50 mmol) conc. sulphuric acid (0.16 ml, 2.9 mmol) was added, the mixture was heated to 80 °C for 30 min, volatiles were stripped off in vacuum, the residue was twice extracted into CH_2Cl_2 (10 ml), combined extracts were passed through a short column of silica gel (i.d. 10 mm, length 50 mm), the filtrate was concentrated to 10 ml, covered with hexane (20 ml) and left for 3 days; bright orange prisms of **4** separated; 0.43 g (53.4%).

*2.6.3. From **3**-Cs salt*

As above, but with **3**-Cs salt (1.5 g, 3.9 mmol) instead of **2**-Cs salt; the yield of **4** was 0.98 g (83.1%).

8,8′-μ-Methylcarboniodioxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate, **4**: m.p. > 300 °C, m/z_{max} 384 (corresponding to $[^{11}B_{18}^{12}C_6^1H_{23}^{16}O_2^{59}Co]^+$); Anal. Calc. for $B_{18}C_6H_{23}O_2Co$:B 51.11%, found 50.82%. HPLC k' value = 4.53. ^{1}H-NMR ($CDCl_3$):4.32 ppm (s, 4H; $CH_{carbor.}$); 2.78 ppm (s, 3H; $CH_3C^+O_2<$). ^{11}B-NMR: ppm (J_{B-H})[^{1}H-{^{11}B}selectively decoupled] ($B_{(assign)}$): 20.85 (s)($B_{(8,8')}$); −1.39 (142) [2.880] ($B_{(10,10')}$); −5.21 (142) [2.338] ($B_{(9,9',12,12')}$); −9.74 (154) [2.818] ($B_{(4,4',7,7')}$); −17.59 (162) [1.714] ($B_{(5,5',11,11')}$); −26.25 (166) [1.643] ($B_{(6,6')}$).

Crystalline solvate **4-benzene** 1:1. From a hot solution of **4** (1.0 g) in benzene (10 ml) lustrous golden leaflets separated upon cooling down; they were filtered, dried in air and examined by ^{1}H-NMR in deuterioacetone: 7.36 ppm (m, 6H; Ar, C_6H_6); 4.32 ppm (s, 4H; $CH_{carbor.}$), 2.777 ppm (s, 3H, CH_3).

*2.7. Preparation of the **3**-salts*

*2.7.1. By solvolysis of **4***

To a suspension of **4** (7.64 g, 20 mmol) in aqueous 50% EtOH (50 ml), kept on a water bath (80 °C), conc. HCl was added (1 ml). Under occasional shaking a homogeneous solution of the **3** conjugate acid was obtained within ca. 30 min.; upon addition of 10% excess of either CsCl (3.8 g in 10 ml H_2O) or $Me_3N{\cdot}HCl$ (2.1 g in 10 ml H_2O) or Et_3N (2.5 ml) and cooling overnight the respective salts separated in a nearly quantitative yield. All can be best crystallised from MeCN in an 80 °C water bath by slow addition of two volumes of $CHCl_3$ and cooling overnight; about 10 ml of MeCN is required per 1 g of the **3**-salt. In all cases dark orange–red leaflets were obtained.

*2.7.2. By direct hydroxylation of **1***

A stirred suspension of **1**-Cs (4.0 g, 8.8 mmol) in 80% aqueous sulphuric acid (100 ml) was heated in a 140 °C bath with gradual dissolution of the major part of solids. The reaction was monitored in 30 min intervals by HPLC with UV detection at 302 nm; when compound **2** was no more detectable (after 24 h), the mixture was cooled down. At this moment the product contained 94% of **3** and 6% of two other anions with k' values < 1.0. The mixture was diluted with water (100 ml), the conjugate acids were extracted three times with Et_2O (30 ml portions). To the combined ether extracts water (20 ml) was added and Et_2O was stripped off along with ca. 5 ml of water. To the clear orange solution $CaCl_2$ (1.1 g, 10 mmol, in 10 ml of water) was added and excess water was evaporated in vacuum until the salt began to solidify; the residue was heated to 80 °C and EtOH (ca. 15 ml) was gradually added to obtain a homogeneous solution. After standing overnight 2.55 (84%) of a microcrystalline yellow **3**-$Ca_{1/2}$ was isolated. It can be easily converted to the more convenient **3**-$HNMe_3$ salt with a slight excess of $Me_3N{\cdot}HCl$ in hot 50% aqueous EtOH.

*2.8. General properties of the **3**-salts*

All salts are insoluble in dry Et_2O, CH_2Cl_2, $CHCl_3$ and water. In contrast to analogous **1**- and **2**-salts they are nearly insoluble in MeCN–$CHCl_3$ (1:2 v/v). In neat MeCN, acetone and hot EtOH, they dissolve well. Their TLC R_F values follow the same pattern as do the corresponding **1**- and **2**-salts; on average they move still more slowly than the preceding salts. For example $R_{F\text{-}HNMe3} = 0.12$ (MeCN–$CHCl_3$ 1:2 v/v), i.e. only 33% of that of **1**-$HNMe_3$ salt ($R_F = 0.36$).

Trimethyl ammonium 8,8′-di-hydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate, **3**-$HNMe_3$ salt: m.p. 296–299 °C, $m/z = 359$, corresponding to the $[^{11}B_{18}^{12}C_4^1H_{22}^{16}O_2^{59}Co]^-$ ion, m/z_{max} (100%) = 356.2; Anal. Calc. for $B_{18}C_7H_{32}O_2NCo$: B 46.79%, found 46.64%. HPLC k' value = 1.05; ^{1}H-NMR (in deuteroacetone)): 6.44 ppm (broad s, 1H; HN^+); 3.71 ppm (s, 4H; $CH_{carbor.}$); 3.1 ppm (s, 9H $(CH_3)_3N^+$). ^{11}B-NMR: ppm (J_{B-H}) [^{1}H-{^{11}B} selectively decoupled] ($B_{assign.}$): 25.82 (s) ($B_{(8,8')}$); −4.56 (162) [2.538] ($B_{(10,10')}$); −5.62 (146) [2.114] ($B_{(9,9',12,12')}$); −8.61 (146) [2.898] ($B_{(4,4',7,7')}$); −19.84 (153) [1.540] ($B_{(5,5',11,11')}$); −29.61 (154) [1.380] ($B_{(6,6')}$).

2.9. X-ray diffraction analysis

Crystal data for **4**: $C_6H_{23}B_{18}CoO_2$, M = 380.75, orthorhombic, $P2_12_12_1$ (No 19), $a = 10.7670(6)$ Å, $b = 13.1850(6)$ Å, $c = 13.0840(7)$ Å, $V = 1857.44(17)$ Å^3, $D_x = 1.362$ Mg m^{-3} for $Z = 4$. A deep orange crystal of dimensions $0.37 \times 0.37 \times 0.45$ mm was mounted on glass capillary with epoxy glue and measured Nonius KappaCCD diffractometer with the graphite monochromator, (Mo–K_α radiation, $\lambda = 0.71073$ Å) at room temperature. A total of 9133 reflections were measured in the range $h = -12$ to 12, $k = -15$ to 15, $l = -15$ to 15, from which 3162 were unique ($R_{int} = 0.052$) and 2986 were regarded as observed according to the $I > 2\sigma(I)$ criterion. Absorption was neglected ($\mu = 0.921$ mm^{-1}). The structure was solved by direct methods and refined by full-matrix least squares based on F^2 (SHELXL97) [15]. The hydrogen atoms were found on difference Fourier map and refined isotropically except for the methyl ones, which were fixed into idealised positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.5\ U_{eq}$(pivot atom). The refinement converged to $R = 0.033$ for observed reflections and $wR = 0.081$, GOF = 1.134 for 327 parameters and all 3162 reflections. The final difference map displayed no peaks of chemical significance (largest difference peak/hole: 0.538/−0.319 e Å^{-3}). The absolute structure was determined unambiguously since chiral parameter is equal to zero within its esd (chiral parameter = 0.000(19)).

3. Results and discussion

3.1. Reductive acetoxylation

In order to clarify the reaction path of reductive acetoxylations of **1** we performed a set of small scale experiments in which 1 mmol of anion **1** was treated with acetic anhydride with/or without co-presence of acetic acid, with/or without strong acid as catalysts, and under various reaction temperatures. Changes were monitored using TLC and eventually, the reaction mixtures were hydrolysed and the composition of final products in the mixture was quantified by HPLC. Concentrated sulphuric acid was used through this study, instead of perchloric acid (see Section 2), for both, practical and safety reasons. The results indicated following features:

(a) without a strong acid no reaction was observed with either acetic anhydride or acetic acid or a mixture of both even at 80 °C for several hours;
(b) no reaction took place with acetic acid and sulphuric acid if acetic anhydride was absent;
(c) a mixture of **1** + acetic acid + acetic anhydride + sulphuric acid, 2 h at 80 °C, afforded 72% of **2**;
(d) a mixture of **1** + acetic anhydride + sulphuric acid without acetic acid, 2 h at 80 °C, gave 61% of **3**; before hydrolysis much **4** was spotted on TLC;
(e) in all reactions leading to **2** or **3** about 30% of **1** was transformed to undefined side products;
(f) treatment of **2** or **3** with acetic anhydride and sulphuric acid led to **4** in 53 and 83% yields respectively.
(g) under conditions sub c,d) a distinct purple red spot (the fastest of all on TLC) was observed corresponding to the already described [8,8′-μ-EtO<(1,2-$C_2B_9H_{10}$)$_2$-3-Co]^0 zwitterion [16,17].

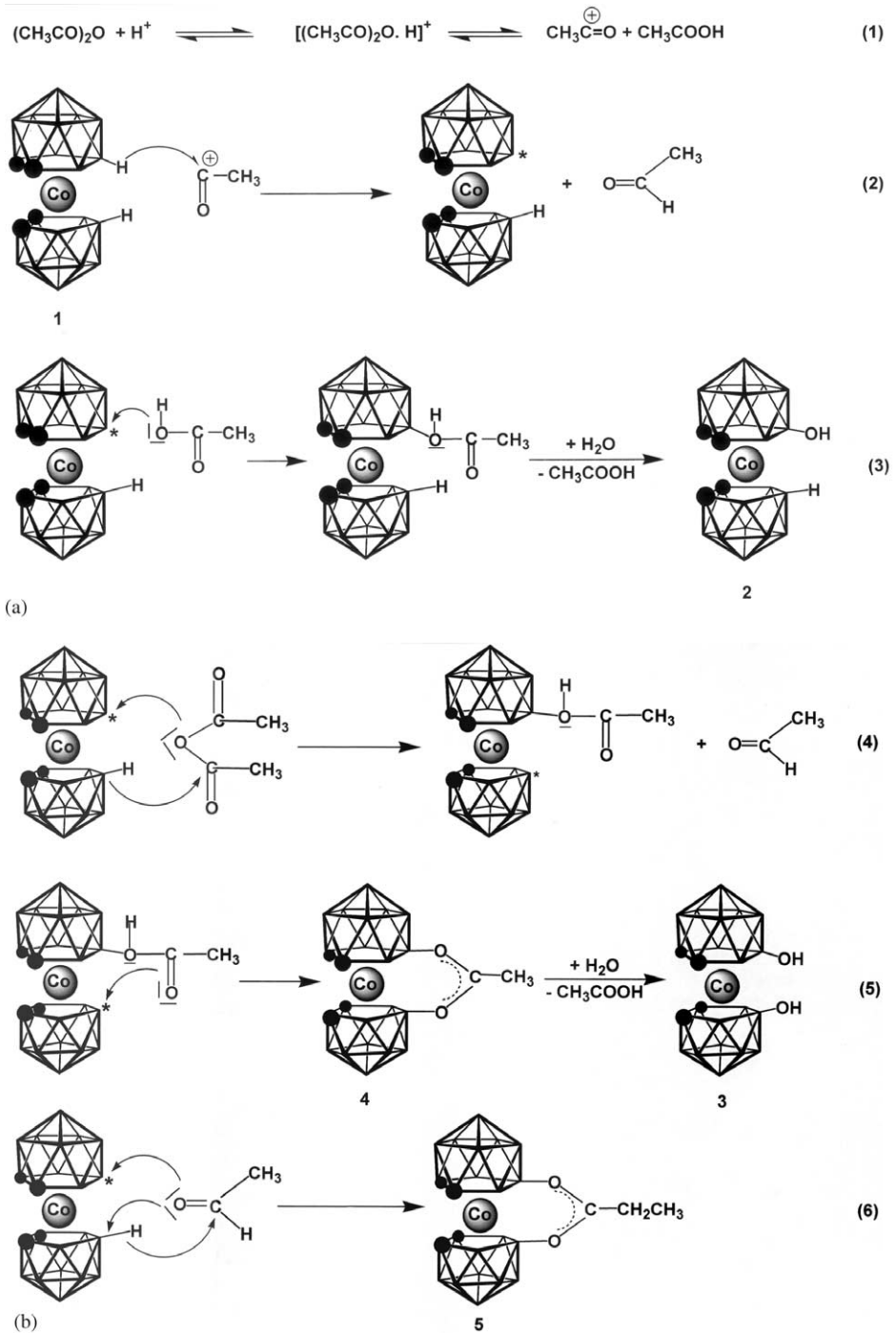
The preliminary experiments have thrown more light on the reaction course of reductive acetoxylations of **1** (see below), and clearly denied the originally proposed reaction mechanism reported in the older paper [8]. This consequently led to development of preparative procedures suitable for large scale syntheses of **2** and **3**. What probably happens is shown in Scheme 1A and B.

The first equation in Scheme 1A shows the essential role of both, acetic anhydride and the strong acid. Hydride ion abstraction and transient formation of the reactive B-intermediate (*designates the empty terminal orbital) is apparent from Eq. (2). Reaction of this intermediate with acetic acid in Scheme 1A gives eventually rise to target anion **2** (Eq. (3)) and explains the beneficial role of acetic acid in this case. The reaction of the same intermediate with acetic anhydride (Scheme 1B) gives **4** (Eqs. (4) and (5)). In this case acetic acid dramatically decreases its yield. Finally, the reaction of the key intermediate with acetaldehyde, followed by another H^- transfer [16,17], is the source of the minor (<1%) side product **5**. Note that the *-designated moieties are uncharged because they arose on an H^- ion abstraction from a monoanion.

The orange zwitterion **4** is the key intermediate in synthesis of **3**. It can be isolated directly from the mixture resulting on heating **1** with acetic anhydride and sulphuric acid to 80 °C, but is still better accessible from pure **3**-salts by a short treatment with acetic anhydride and sulphuric acid at 80 °C. This is a reversal of the second part of Eq. (5); **4** was already reported

and, although it was not fully characterised, its correct constitution was proposed [8]. Now we confirm it by X-ray structure (Fig. 1); selected distances and angles are summarised in Table 1.

The non-solvated compound **4** crystallises only from dichloromethane, from which orange prisms were grown for X-ray measurement; this species is much more soluble in hot benzene, from which it crystallises in the form of golden leaflets, containing one molecule of benzene (found by ^{1}H-NMR in deuterioacetone).



Scheme 1. A. The probable reaction path to hydroxyderivative **2** showing the essential role of both, acetic anhydride and the strong acid. Hydride ion abstraction and transient formation of the reactive zwitterionic B-intermediate (asterisk (*) indicates vacant terminal orbital on the $B_{(8)}$ atom) is apparent from Eq. (2). Reaction of this intermediate with acetic acid eventually gives rise to target anion **2** (Eq. (3)) and explains the beneficial role of acetic acid in this case. B. The probable reaction path leading to dihydroxyderivative **3**. The reaction of the same intermediate as in A (asterisk (*) indicates vacant terminal orbital) with acetic anhydride gives bridged by-product **4** (Eqs. (4) and (5)). The moieties marked with asterisk in position $B_{(8)}$ are uncharged, because they arose on a H^- ion abstraction from a monoanion.

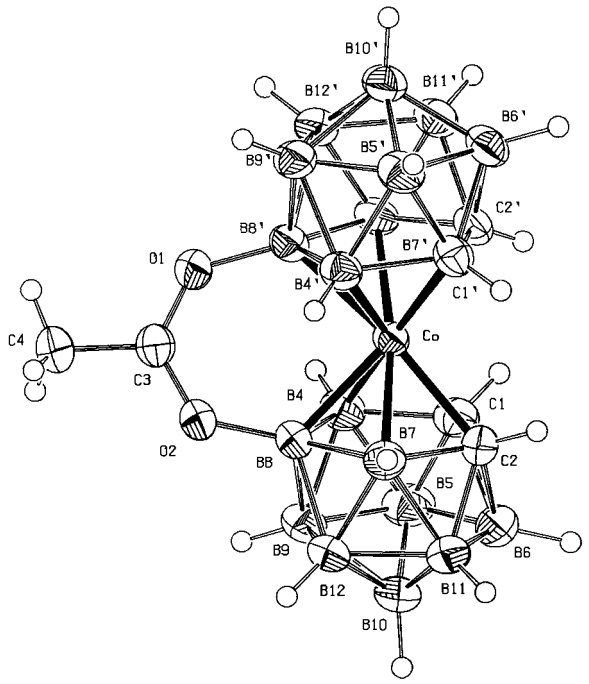


Fig. 1. Molecular structure of **4** showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Selected interatomic distances and angles

Distance (Å)		Angle (°)	
Co–B8′	2.058(4)	B8′–Co–B8	89.42(14)
Co–B8	2.065(3)	O1–B8′–Co	119.9(2)
B8–O2	1.476(4)	O2–B8–Co	120.7(2)
B8′–O1	1.487(4)	C3–O2–B8	127.3(3)
O1–C3	1.266(4)	C3–O1–B8	127.9(3)
O2–C3	1.274(4)	O1–C3–C4	118.2(3)
C3–C4	1.474(4)	O2–C3–C4	117.2(3)
		O1–C3–O2	124.6(3)

The originally reported 'golden yellow crystals' in Ref. [8] were apparently this solvate. The compound is rather sensitive to solvolysis because it slowly decomposes at the silica gel on TLC during sheet development leaving a long yellow tail behind the main spot.

Acid solvolysis of **4** in ca. 50% ethanol is very fast, quantitative, and it is the best way to the synthesis of pure **3**-salts in preparative scale. These precipitate from the crude hydrolysate upon addition of bulky cations such as Cs^+, R_3N, etc.

3.2. Direct hydroxylation in sulphuric acid

Above encouraging results along with the recently reported case of direct hydroxylations of divalent anion $[B_{12}H_{12}]^{2-}$ [18] prompted us to investigate the same reaction with **1**, although this ion is well known for its resistance to strong non-oxidising acids [3].

Indeed, cobaltacarborate anion **1** reacts with diluted sulphuric acid producing hydroxyderivatives **2** and **3**. The course of the reaction was studied and the conditions leading to the anions **2** and **3** optimised using HPLC analysis of the respective reaction mixtures. Conditions necessary for formation of hydroxyderivatives are: concentration of H_2SO_4 above 60% and at temperatures higher than ca. 120 °C. Apparently, reaction proceeds through the stage of the monosubstitution and subsequently leads to disubstituted derivative. On the other hand, when the starting compound disappeared completely, dihydroxyderivative was always present in the reaction mixture in quantities ranging from 15 to 20%. Reasons for presence of this compound would be relatively fast kinetics, and low solubility of Cs^+**1** salt or even the conjugate acid $H_3O^{(+)}$**1** in 60% sulphuric acid. Reaction is heterogenous even if carried out in a larger volume of the acid. The monohydroxyderivative was obtained from this mixture by crystallisation of the cesium salts in reasonable isolable yield (61%) and good purity ($>95\%$). The route to dihydroxyderivative is more straightforward especially in respect of its isolation. Heating of the Cs^+**1** in 80% H_2SO_4 at 140 °C for 24 h (or 48 h in 60% H_2SO_4) produces almost pure dihydroxyderivative which may be purified by crystallisation in the form of Ca^{2+} salt. Prolonged treatment at this temperature leads to presence of impurities with lower HPLC k' values. Isolation of the hydroxyderivatives of the univalent cation **1** from excess of sulphuric acid is simple. The products could be extracted into diethyl ether after dilution of the acid and transferred in the form of conjugate acids into water and precipitated by bulky cations and recrystallised.

We are not sure, whether it is a true 'direct hydroxylation', in which case hydrogen should evolve, or whether it is just another 'reductive hydroxylation' on account of reduction of a part of sulphuric acid to sulphur dioxide. This route forms rather a viable alternative with respect to diol species **3** synthesis; use of this procedure for larger production of pure anion **2** seems more tedious than the above reductive acetoxylation method (see Section 2).

A graphic depiction of results summary is shown in Scheme 2.

3.3. NMR spectroscopy

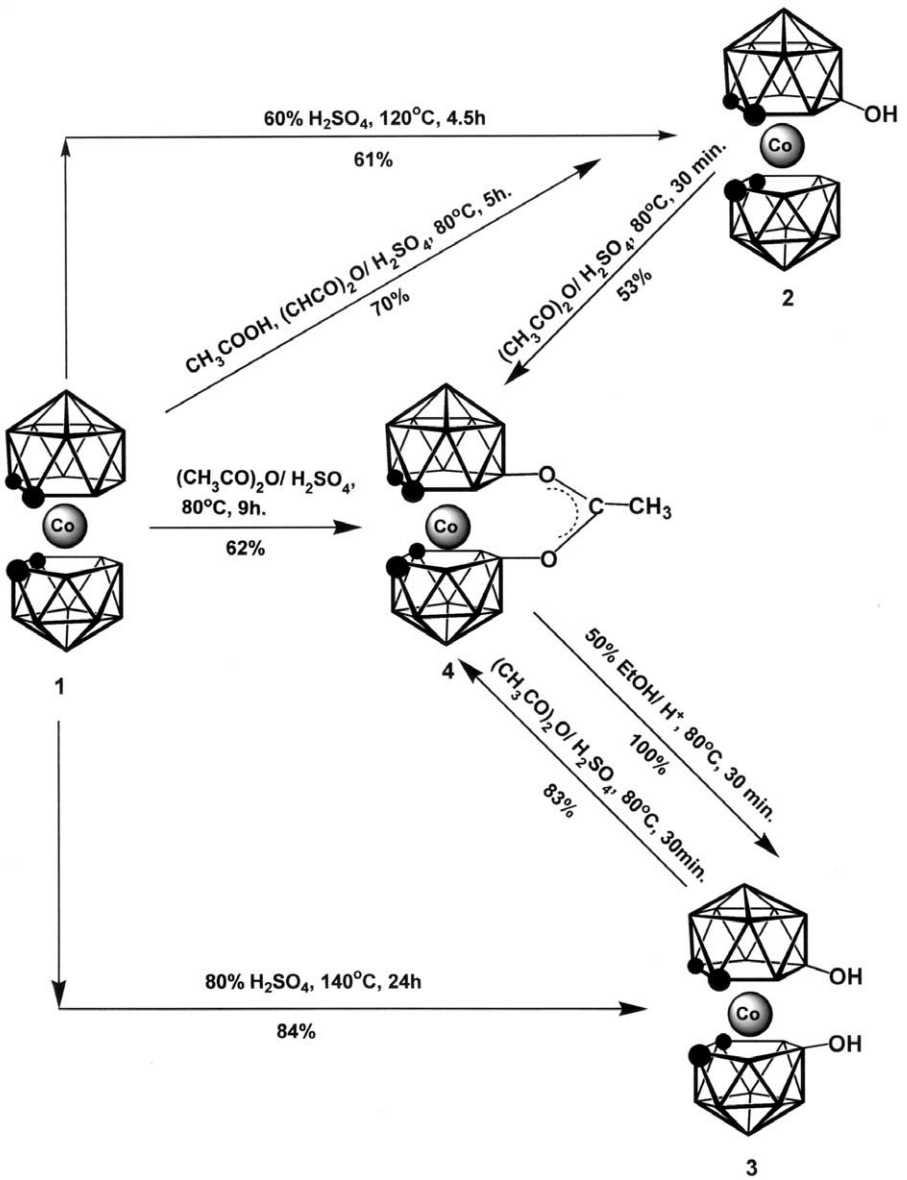
All isolated compounds were unequivocally characterised by MS, HPLC and NMR with a complete assignment of all ^{1}H. ^{11}B-NMR patterns of derivative **2** consists of 12 peaks, one singlet of relative intensity 1 which is the first peak in the spectrum and 11 doublets of intensities 1:1:1:2:2:2:2:2:2:1:1. This is in agreement with the expected spectral pattern for the substitution in the position B(8) of the cage leaving the existence of

one plane in the molecule provided that the free rotation around the central cobalt atom is preserved in solution. Spectrum consists of two sets of signals for individual carborane ligand parts, one perturbed by B–O–X substitution and second almost unchanged compared to that of parent unsubstituted anion **1**. All signals corresponding to these two individual carborane parts can be clearly distinguished on the basis of crosspeaks in the $^{11}B–^{11}B$ COSY experiments and assigned to respective boron positions. Also, all B–H signals could be assigned from the $^{1}H\{^{11}B(selective)\}$ experiments.

^{11}B-NMR spectra of the diol **3** and the bridge derivatives **4** consist of one singlet with relative intensity 2 which is the first peak in the spectrum and five doublets of intensities 2:4:4:4:2. Both, the spectral pattern and chemical shifts reflect the same symmetry equivalence (in case **4** only seemingly, due to its asymmetric twisted structure) of two carborane ligands. All signals corresponding to individual boron resonances could be unambiguously assigned to respective boron positions from the $^{11}B–^{11}B$ COSY experiments. Also, all B–H signals could be assigned from the $^{1}H\{^{11}B(selective)\}$ experiments. For NMR details see Section 2.

3.4. X-ray crystallography

The structure of **4** (Fig. 1) displays structural features similar to analogous three atom bridged moieties in anions $[X–P(O)(O)_2<(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^-$ ($X = Cl$, Et_2N) prepared recently starting from diol **3** [7]. The least-square planes defined by pentagons C(1), C(2),



Scheme 2. The overall reaction routes leading to the anions **2** and **3** and the zwitterionic by-product **4** in preparative scale.

B(4),B(7),B(8) (**pl**) and C(1)′, C(2)′, B(4)′,B(7)′,B(8)′ (**pl′**) are also almost parallel (4.6(2)°) and the position of Co atom with regard of dicarbollide ligands remains unaffected by the bridge, the angle cg–Co–cg′ (cg = centroid of pentagon C(1), C(2), B(4), B(7), B(8)) is very close to 180° (177.7°). The torsion angle φ: B(8)–cg–cg′–B(8′), characterising antiprismatic arrangement of ligands is equal −22.6°, whereas in two previously reported compounds [8,8′-μ-ClP(O)$(O)_2$<(1,2-$C_2B_9H_{10})_2$-3-Co]HN-$(C_2H_5)_3$ and [8,8′-μ-Et_2NP(O)$(O)_2$<(1,2-$C_2B_9H_{10})_2$-3-Co] HN$(CH_3)_3$ is −30.91 and 26.01°, respectively. The CH_3C^+<O_2 moiety is planar (the largest deviation from least-square plane through atoms C(4), C(3), O(1) and O(2) (**pl2**) is equal 0.003 Å) and **pl2** plane is inclined towards planes of pentagons **pl** and **pl′** by dihedral angles 64.8 and 64.2°, respectively. The atoms B(8) and B(8′) are displaced from plane **pl2** each on one side by 0.34 and −0.38 Å, respectively, to achieve antiprismatic arrangement. It should be pointed out, similarly as in the [8,8′-μ-Et_2NP(O)$(O)_2$<(1,2-$C_2B_9H_{10})_2$-3-Co]$^-$ anions, one enantiomer of **4** separated by crystallisation was successively selected from the crystal mixture. The absolute configuration of this enantiomer was determined and its configuration can be designated as the [σ,σ-8,8′-μ-CH_3CH(O)$_2$<(1,2-$C_2B_8H_{10})_2$-3-Co]^0, according to the numbering scheme suggested and published in our previous articles describing chemistry of chiral metallacarbaboranes [19]. Since skeletal bond lengths and angles fall within the usual range typical for the cobalta bis-dicarbollide series [19–22], only selected data for the bridge atoms and attached cluster boron atoms are summarised in Table 1.

4. Conclusions

A long standing problem in the development of more efficient selective extraction agents based on **1** has been the limited availability of suitable derivatives of this anion containing simple reactive functionalities which could be modified by subsequent high yield reactions thus producing anions with good chemical and radiolytical stability. The present work remarkably improves the synthetic routes to hydroxyderivatives of anion **1** which are particularly attractive with respect to their well known potential to be modified with a large variety of selective groups. Two alternative procedures depicted in Scheme 2 are presented which both provide the mono-**2** and dihydroxyderivative **3** of the anion **1** in preparative scale. The simple and high yield syntheses outlined above enormously facilitated the access to the diol **3**. The deeper understanding of the reductive acetoxylation reaction paths, published here for the first time, accounts for preparative availability of the anion **2**. This can be exemplified by the fact that several tens of grams of the respective salts of ions **2** and **3** were prepared in our laboratory during the past 2 years, either via reductive acetoxylation of **1**, or more recently by direct hydroxylation. As expected, these compounds have proven to serve as useful starting materials for synthesis of derivatives of anion **1** bearing either phosphorus containing moieties [7] or crown ether rings [23], with properties tailored for solvent extractions of radionuclides [6].

The stereochemistry of the bi-polar compound **4** with asymmetric twisted structure introduced by steric requirements of the bridge substituent is noteworthy . This compound represents, along with recently reported results [7], another example of chiral bridged derivative of **1**, where one pure enantiomer was separated by successive crystallisation, and its absolute configuration was unambiguously determined by X-ray crystallography.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171058 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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