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Stability of nickel bis(dicarbollide) complexes

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Nickel bis(dicarbollide) complexes [3,3'-Ni(IV)(1,2-$C_2B_9H_{11})_2$] [1], Cs[3,3'-Ni(III)(1,2-$C_2B_9H_{11})_2$] [S1], [H(Phen)$_2$][3,3'-Ni(III)(1,2-$C_2B_9H_{11})_2$] [S2] and [6,6'-Ph$_2$-3,3'-Ni(IV)(1,2-$C_2B_9H_{11})_2$] [S3] were prepared as described in literature. All reactions were carried out in air. The reaction progress was monitored by thin-layer chromatography using Merck F254 silica gel on aluminum plates. Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C) were recorded with a Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using $BF_3 \cdot Et_2O$ as external standard.

Reaction of [3,3'-Ni(1,2-$C_2B_9H_{11})_2$] with 2,2'-bipyridine in ethanol.

In typical experiment, a solution of 2,2'-bipyridine (625 mg, 4 .0 mmol) in ethanol (10 ml) was added to solution of [3,3'-Ni(IV)(1,2-$C_2B_9H_{11})_2$] (315 mg, 1.0 mmol) in ethanol (30 ml) and stirred at ambient temperature for 3 h observing the change of the reaction mixture color from orange to marsh green. TLC monitoring of the reaction mixture on silica with dichloromethane as eluent detected complete disappearance of the starting nickel(IV) complex, whereas the ^{11}B NMR spectroscopy revealed their reduction to the paramagnetic Ni(III) complex [3,3'-Ni(III)(1,2-$C_2B_9H_{11})_2$]$^-$. The reaction mixture was left overnight. The brown precipitate formed was separated by filtration; according to the ^{11}B NMR spectroscopy, the precipitate contained mainly nickel(III) bis(dicarbollide) [3,3'-Ni(III)(1,2-$C_2B_9H_{11})_2$]$^-$ as well as some amount of the nickel(II) complex [3-Bipy-3,1,2-Ni$C_2B_9H_{11}$]. The filtrate contained nickel(III) bis(dicarbollide) and traces of *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$. The repeated crystallization of the precipitate from hot acetone gave 42 mg (12% yield) of [3-Bipy-3,1,2-Ni$C_2B_9H_{11}$]. ^{11}B{^{1}H} NMR (acetone-*d*$_6$, ppm): -3.3 (1B), -10.1 (2B), -11.2 (1B), -16.0 (2B), -20.4 (2B), -21.6 (1B); ^{1}H NMR (acetone-*d*$_6$, ppm): 8.59 (2H, d, *J* = 8.0 Hz, *Bipy*), 8.28 (2H, d, *J* = 8.0 Hz, *Bipy*), 8.25 (2H, t, *J* = 7.4 Hz, *Bipy*), 7.65 (2H, t, *J* = 7.4 Hz, *Bipy*), 2.36 (2H, s, C*H*$_{carb}$); ^{13}C NMR (acetone-*d*$_6$, ppm): 153.3 (*Bipy*), 138.1(*Bipy*), 125.7 (*Bipy*), 122.3 (*Bipy*), 23.6 (*C*$_{carb}$).

The filtrate was left aside for 1 week and evaporated to dryness *in vacuo*. The ^{11}B NMR spectroscopy revealed the presence of two different *nido*-carboranes, the parent one and symmetrically substituted in molar ratio ~ 4 : 5. The fractional recrystallization from hot ethanol gave 230 mg (26% yield) of $[Ni(Bipy)_3][3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]_2$. ^{11}B NMR (acetone-$d_6$, ppm): -1.4 (1B, s), -12.5 (2B, d, *J* = 134 Hz), -18.3 (2B, d, *J* = 129 Hz), -23.4 (2B, d, *J* = 144 Hz), -39.0 (1B, d, *J* = 158 Hz), -40.7 (1B, d, *J* ~ 120 Hz); ^{1}H NMR (acetone-d_6, ppm): 3.64 (2H, m, OCH_2CH_3), 1.81 (2H, s, CH_{carb}), 1.08 (3H, m, OCH_2CH_3), -2.77 (1H, br s, BHB).

In another experiment, a solution of $[3,3'\text{-}Ni(IV)(1,2\text{-}C_2B_9H_{11})_2]$ (63 mg, 0.2 mmol) and 2,2'-bipyridine (156 mg, 1.0 mmol) in ethanol (40 ml) was heated under reflux for 5 h. The reaction mixture was allowed to cool to ambient temperature and concentrated to dryness under reduced pressure. The ^{11}B NMR spectroscopy revealed the presence of $[7,8\text{-}C_2B_9H_{12}]^-$ and $[3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]^-$ in the molar ratio 1 : 1.

Reaction of $[H(Phen)_2][3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{11})_2]$ with ethanol.

$[H(Phen)_2][3,3'\text{-}Ni(III)(1,2\text{-}C_2B_9H_{11})_2]$ (136 mg, 0.2 mmol) in ethanol (100 ml) was heated under reflux for 5 h. The reaction mixture was allowed to cool to ambient temperature and concentrated to dryness under reduced pressure. The ^{11}B NMR spectroscopy revealed the presence of $[7,8\text{-}C_2B_9H_{12}]^-$ and $[3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]^-$ in the molar ratio ~ 1 : 1.

Reaction of $Cs[3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{11})_2]$ with ethanol.

A solution of $Cs[3,3'\text{-}Ni(III)(1,2\text{-}C_2B_9H_{11})_2]$ (46 mg, 0.1 mmol) in ethanol (50 ml) was heated under reflux for 7 h. The mixture was allowed to cool to ambient temperature and concentrated to dryness under reduced pressure. The ^{11}B NMR spectroscopy revealed the presence of $[7,8\text{-}C_2B_9H_{12}]^-$ and $[3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]^-$ in the molar ratio ~ 1 : 1.

Reaction of $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{10})_2]$ with 1,10-phenanthroline in ethanol.

A solution of $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Ni(IV)(1,2\text{-}C_2B_9H_{11})_2]$ (70 mg, 0.15 mmol) and 1,10-phenanthroline (108 mg, 0.60 mmol) in ethanol (100 ml) was heated under reflux for 7 h. The mixture was allowed to cool to ambient temperature and concentrated to dryness under reduced pressure. The ^{11}B NMR spectroscopy revealed the presence of the paramagnetic Ni(III) complex $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Ni(III)(1,2\text{-}C_2B_9H_{11})_2]^-$ as the single product. The residue was dissolved in acetonitrile (50 ml), treated with a solution of $FeCl_3$ (80 mg, 0.50 mmol) in acetonitrile (10 ml) and stirred at ambient temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica with dichloromethane as eluent to obtain $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Ni(IV)(1,2\text{-}C_2B_9H_{11})_2]$ (58 mg, 83 %).

Single crystal X-ray study of anion 4.

Single crystal X-ray study was carried out with SMART APEX II CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. Crystallographic data for $[Ni(Bipy)_3][3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]_2$: $C_{30}H_{24}N_6Ni^{2+}\cdot 2(C_4H_{16}B_9O)^-$ are triclinic, space group *P-1*: a = 10.0956(7) Å, b = 15.1974(11) Å, c = 15.5660(11) Å, α = 74.8000(10)°, β = 79.8710(10)°, γ = 85.221(2)°, V = 2267.0(3) Å^3, Z = 2, M = 882.17, d_{cryst} = 1.292 g·cm^{-3}. $wR2$=0.1117 calculated on F^2_{hkl} for all 13830 independent reflections with $2\theta < 30.5°$, (GOF = 1.042, R = 0.0421 calculated on F_{hkl} for 10743 reflections with $I > 2\sigma(I)$). Crystallographic data (including structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC 1907219.

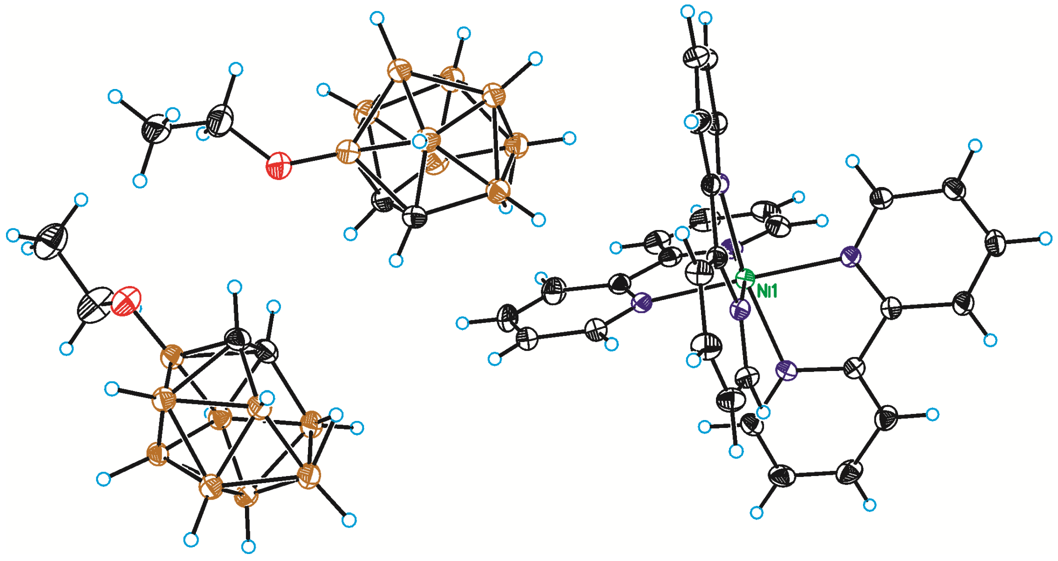

Figure S1. General view of tris(2,2′-bipyridine)nickel(II) bis(3-ethoxyundecahydro-7,8-dicarba-*nido*-undecaborate) $[Ni(Bipy)_3][3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]_2$.

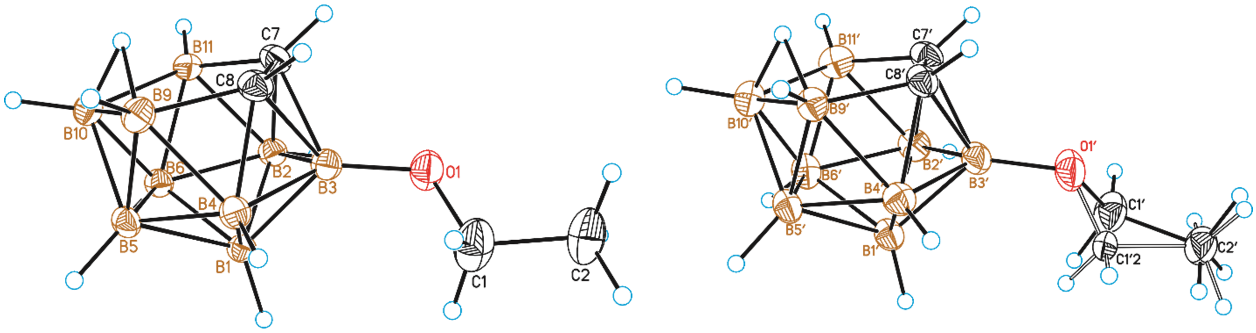

Figure S2. General view of both symmetrically independent anions showing disorder of the primed molecule. Minor part of the disorder is given by open lines. Displacement ellipsoids are drawn at the 50% probability level.

In order to obtain more information on the structural details we have carried out quantum chemical calculations of the isolated anion using the PBE0/6-311G(df,pd) method that was proved to be reliable for calculation of variety of organic and organoelement compounds [S4-S6]. The results have not revealed any intramolecular attractive interactions which would stabilize specific configuration. The calculated geometry somewhat differs from the experimental one (Table S1). Taking into account an absence of intramolecular nonbonded attractive forces, difference between experiment and theory is quite possible and is governed by intermolecular interactions.

Table S1. Ethoxy group orientation in anion [3-EtO-7,8-$C_2B_9H_{11}$]$^-$. Comparison between theory and experiment.

Torsion angle, deg	X-ray	Calculations
B10-B3-O1-C1	138.2	127.87
B10'-B3'-O1'-C1'	150.2	
B10'-B3'-O1'-C1'2	-150.2	

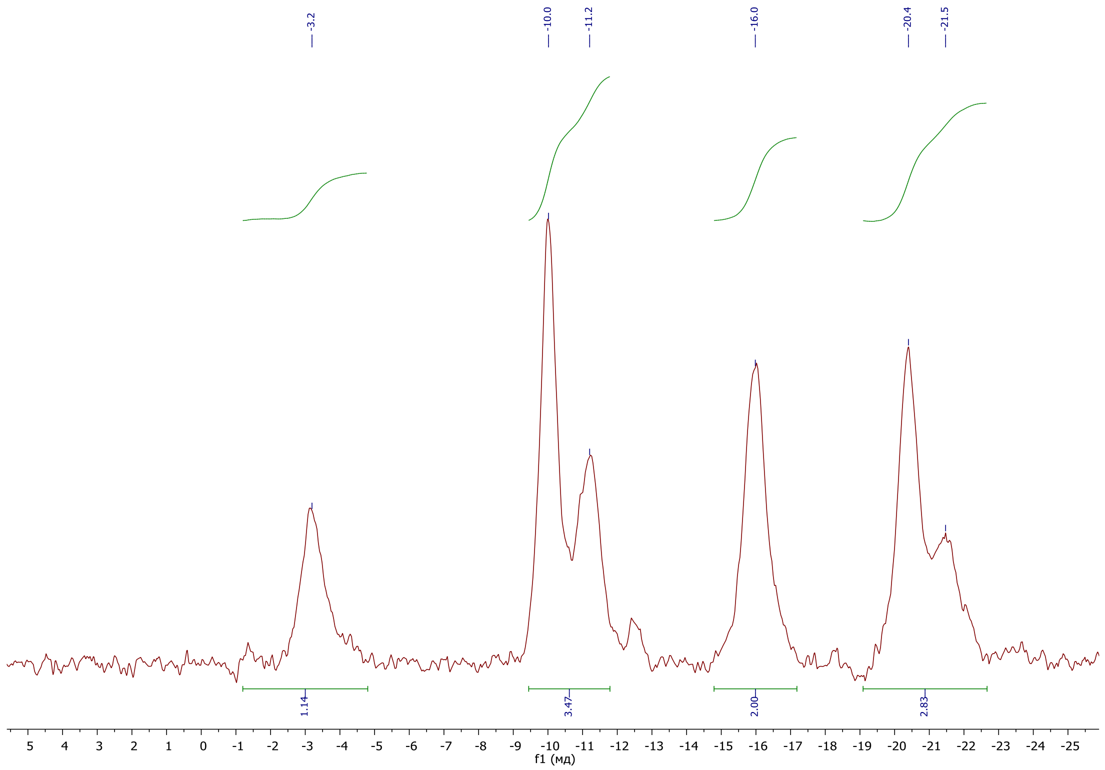

Figure S3. ^{11}B{^{1}H} NMR spectrum of [3-Bipy-3,1,2-NiC$_2$B$_9$H$_{11}$] in acetone-d_6.

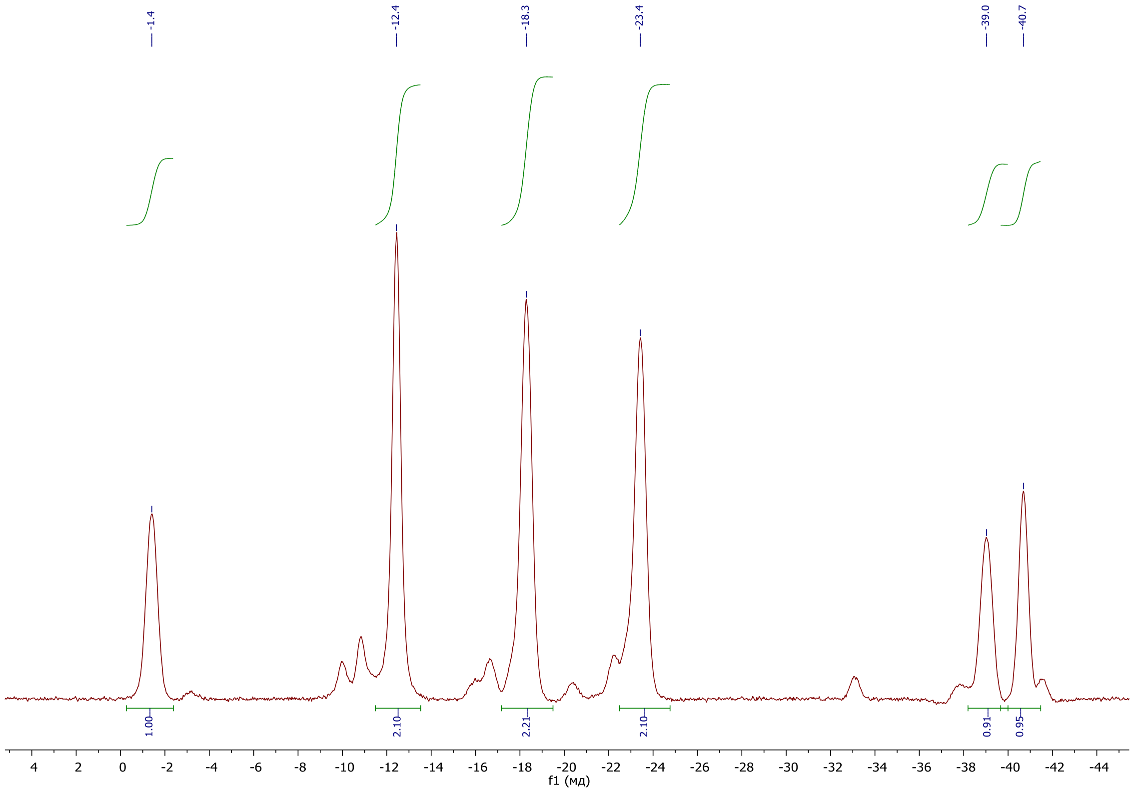

Figure S4. ^{11}B{^{1}H} NMR spectrum of [Ni(Bipy)$_3$][3-EtO-7,8-C$_2$B$_9$H$_{11}$]$_2$ in acetone-d_6.

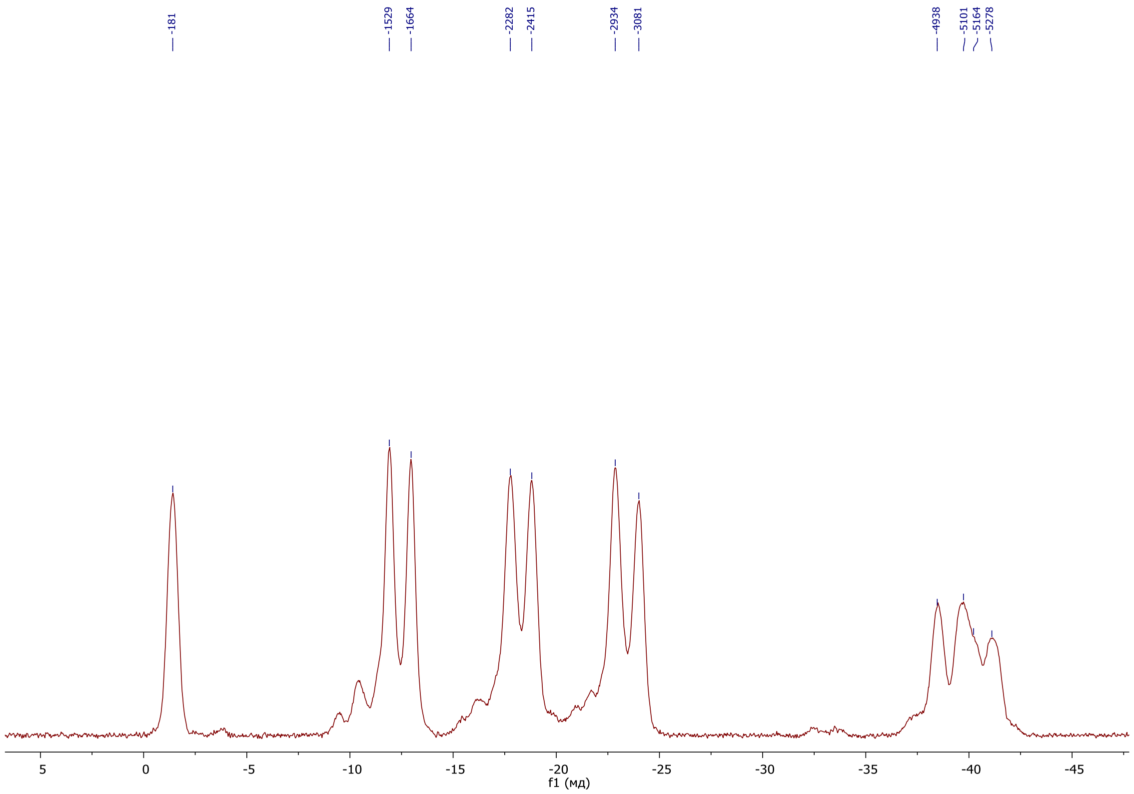

Figure S5. ^{11}B NMR spectrum of $[Ni(Bipy)_3][3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]_2$ in acetone-d_6.

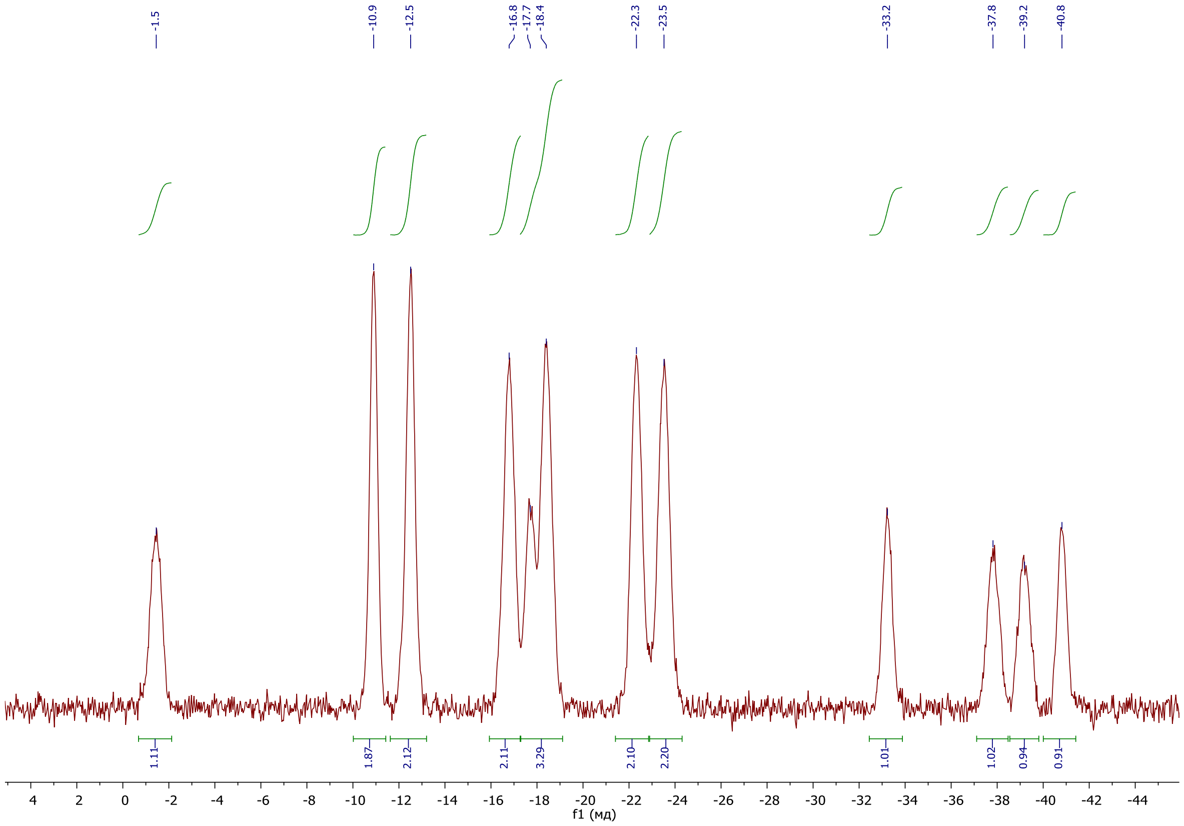

Figure S6. Typical ^{11}B NMR spectrum (acetone-d_6)of mixture of $[3\text{-}EtO\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and $[7,8\text{-}C_2B_9H_{11}]^-$ anions formed on degradation of nickel(IV) and nickel(III) bis(dicarbollides).

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