

Syntheses, structural characterization and CO releasing properties of boranocarbonate $[\text{H}_3\text{BCO}_2\text{H}]^-$ derivatives

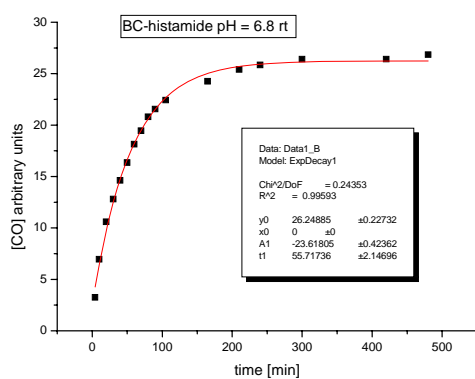
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Supplementary Information

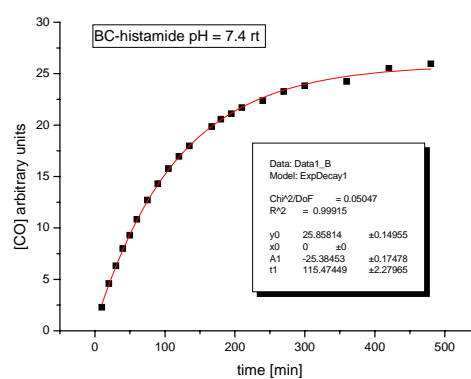
1. Selected CO releasing traces and data fitting

For all compounds, t_1 corresponds to $1/k_{\text{obs}}$ (min) and $t_{1/2} = \ln 2/k_{\text{obs}}$

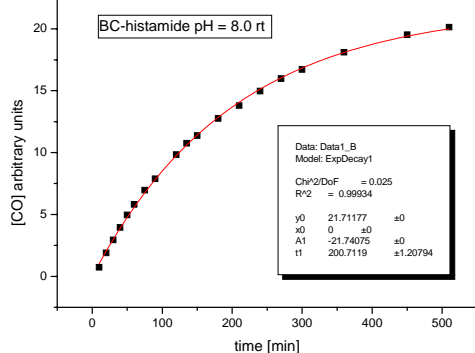
1a) Compound $[\text{Na}(18\text{-crown-6})][\text{H}_3\text{BCOhist}]$ (4)



$t_{1/2} = 39$ min

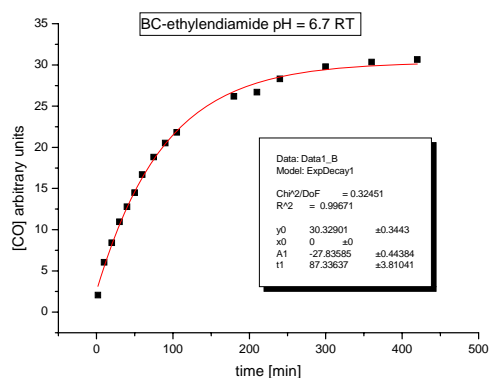


$t_{1/2} = 80$ min

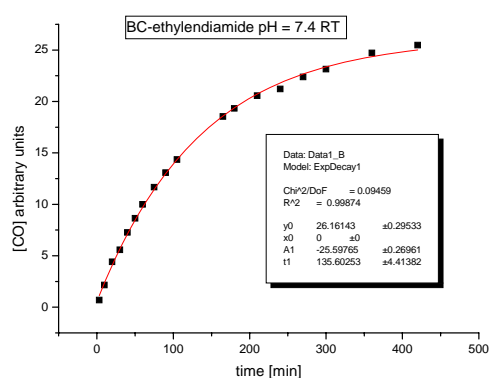


$t_{1/2} = 139$ min

1b) Compound $[\text{Na}(18\text{-crown-6})]_2[(\text{H}_3\text{BCO})_2\text{en}]$ (8)

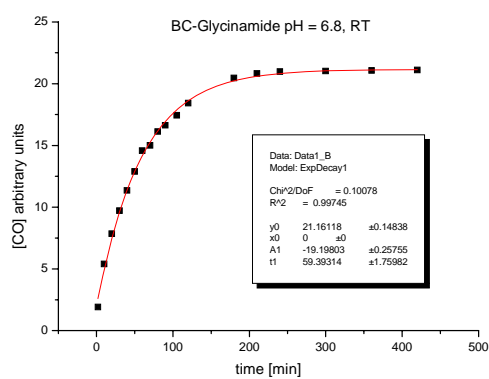


$t_{1/2} = 63$ min

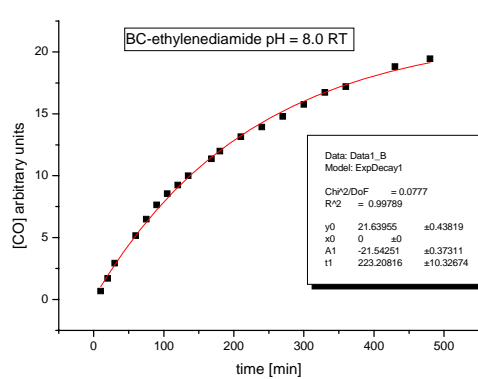


$t_{1/2} = 95$ min

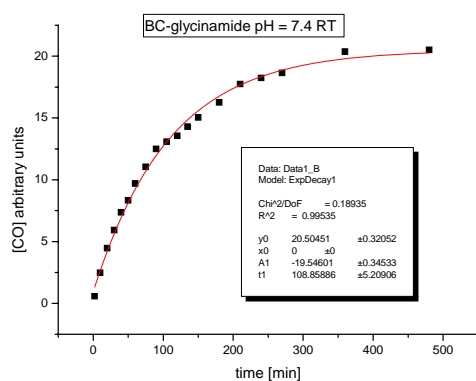
1c) Compound $\text{Na}_2[\text{H}_3\text{BCOgly}]$ (7)



$t_{1/2} = 41$ min

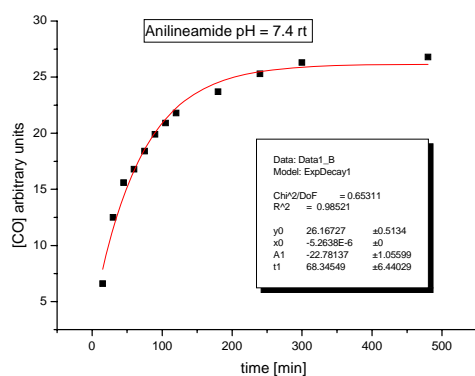


$t_{1/2} = 155$ min



$t_{1/2} = 80$ min

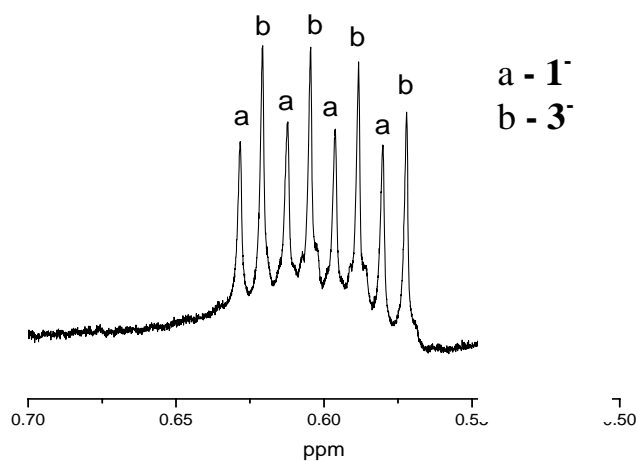
1d) Compound $\text{Na}_2[\text{H}_3\text{BCOani}]$ (**6**)



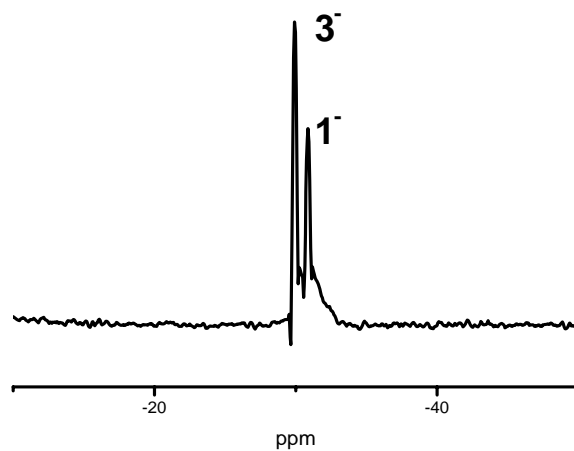
$$t_{1/2} = 46 \text{ min}$$

The curves have been fitted with Origin 6.1. The expression to which the curves were fitted is $y = y_0 + A_1 \cdot \exp(-(x-x_0)/t_1)$

2. ^{11}B and ^1H NMR spectrum during CO release of compound **3**.



^1H NMR spectrum showing two types of $\{\text{BH}_3\}$ fragment during CO release from **3**⁻



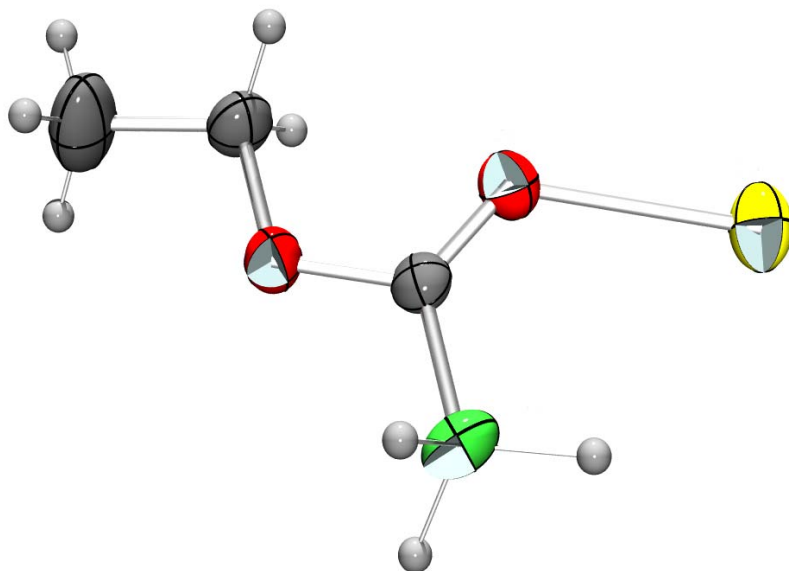
^{11}B NMR spectrum showing two types of ^{11}B during CO release from **3**⁻

3. Crystallographic data

	[Na(18-crown-6)][2]	[Na(18-crown-6)][3]	[K(18-crown-6)][4]	[K(18-crown-6)][6] ^{*1/2} (C ₆ H ₅ NH ₂)	[K(18-crown-6)] ₂ [8]
Empirical formula	C ₁₅ H ₃₂ BNaO ₈	C ₁₇ H ₃₅ BNNaO ₈	C ₁₈ H ₃₅ BKN ₃ O ₇	C ₂₂ H _{36.5} BKN _{1.5} O ₇	C ₂₈ H ₆₀ B ₂ K ₂ N ₂ O ₁₄
Formula weight	374.21	415.26	455.40	483.93	748.60
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Diffractionmeter	Oxford Diffraction Xcalibur Ruby	IPDS 2T Stoe	Oxford Diffraction Xcalibur Ruby	Oxford Diffraction Xcalibur Ruby	Oxford Diffraction Xcalibur Ruby
Wavelength [Å]	0.7107	1.5418	0.7107	0.7107	0.7107
Space group	P2 ₁	P2 ₁ /n	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2	P2 ₁ /n
a [Å]	8.4146(2)	8.0562(3)	8.5561(2)	20.6439(7)	8.5100(2)
b [Å]	18.1567(4)	18.4484(6)	15.6585(4)	14.6541(4)	14.5204(4)
c [Å]	13.8651(4)	15.3958(6)	17.7150(4)	8.4379(3)	15.9909(3)
β [°]	105.663(3)	100.588(3)			95.544(2)
Volume [Å ³]	2039.67(9)	2249.23(14)	2373.38(10)	2552.61(14)	1966.73(8)
Z	4	4	4	4	2
Crystal size [mm ³]	0.50 x 0.10 x 0.10	0.27 x 0.27 x 0.09	0.25 x 0.07 x 0.05	0.52 x 0.09 x 0.06	0.17 x 0.12 x 0.10
Crystal description	white needle	colourless plate	colourless needle	colourless needle	colourless prism
Reflections collected	28939	14351	21375	15585	15706
Independent reflections, R _{int}	6395, 0.0317	3535, 0.0960	5896, 0.0446	5548, 0.0548	3998, 0.0459
Reflections observed [I>2σ(I)]	5074	3063	3384	3227	2040
Completeness to theta	99.8 % to 30.51°	99.0 % to 62.37°	99.9 % to 28.28°	99.9 % to 27.10°	99.6 % to 26.37°
Data / restraints / parameters	6395 / 1 / 457	3535 / 0 / 256	5896 / 0 / 280	5548 / 23 / 307	3998 / 0 / 226

Goodness-of-fit on F^2	1.083	1.097	0.880	0.933	0.991
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0483 wR2 = 0.1014	R1 = 0.0529 wR2 = 0.1479	R1 = 0.0380 wR2 = 0.0580	R1 = 0.0569 wR2 = 0.0848	R1 = 0.0383 wR2 = 0.0774
R indices (all data)	R1 = 0.0680 wR2 = 0.1154	R1 = 0.0589 wR2 = 0.1514	R1 = 0.0872 wR2 = 0.0694	R1 = 0.1202 wR2 = 0.0961	R1 = 0.1097 wR2 = 0.1056
Absolute structure parameter	0.0(3)		0.01(3)	0.08(5)	
Largest diff. peak and hole [$e \cdot \text{\AA}^{-3}$]	0.334 and -0.200	0.272 and -0.233	0.181 and -0.191	0.460 and -0.217	0.225 and -0.271

4. ORTEP representation of Na[2]



Only one out of 2 molecules shown for clarity. The 18-crown-6 was omitted for clarity as well.