

Supporting Information

Transformation of the Ionic Liquid [EMIM][B(CN)₄] into Anionic and Neutral Lanthanum Tetracyanoborate Coordination Polymers by Ionothermal Reactions

Sven H. Zottnick, Maik Finze, Klaus Müller-Buschbaum*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

*Prof. Dr. Klaus Müller-Buschbaum,
Fax: (+)49-931-3184785;
Tel: (+)49-931-3188724,
E-mail: k.mueller-buschbaum@uni-wuerzburg.de

Experimental Details and Methods

Materials. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was purchased from Merck KGaA with a purity of >99.9% and used as purchased. Dichloromethane (Acros, 99.9 %) was also used as purchased. $[\text{EMIM}][\text{B}(\text{CN})_4]$ was prepared according to a procedure described in reference ^[1].

Synthesis of $[\text{La}(\text{NO}_3)_2\text{B}(\text{CN})_4(\text{H}_2\text{O})_4]$ (1). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 43.3 mg) and $[\text{EMIM}][\text{B}(\text{CN})_4]$ (0.3 mmol, 67.8 mg) were mixed in a glass ampoule and subsequently stirred for 30 min at room temperature. Thereafter, the mixture was heated to 75 °C via an oil bath and kept at this temperature for 2 h until a precipitate formed in the heat. The solution was cooled to room temperature overnight and kept in a fridge for 5 days to complete crystallization. The crystals were isolated manually and washed twice with anhydrous dichloromethane (0.20 ml). Yield: 10.40 mg = 23 %. MIR (ATR): (3600 – 3000 b, 1632 m, 1612 m, 1510 m, 1495 m, 1462 m, 1316 m, 1275 s, 1029 m, 960 m, 948 m, 932 m, 813 m, 743 m) cm^{-1} . Elemental analysis for $\text{C}_4\text{H}_8\text{BLaN}_6\text{O}_{10}$ ($M_r = 449.88 \text{ g mol}^{-1}$): calcd. C 10.68; N 18.68; H 1.79 %; found: C 10.97; N 18.55; H 1.89 %.

Synthesis of $[\text{EMIM}]_\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (2). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 66.5 mg) and $[\text{EMIM}][\text{B}(\text{CN})_4]$ (0.45 mmol, 101.7 mg) were placed in a glass ampoule and subsequently stirred overnight at room temperature. Thereafter, the mixture was heated to 80°C via an oil bath until a turbidity was visible and subsequently heated to 120°C in 4h. This temperature was kept for 4 h until a colourless precipitate formed in the heat. The solution was cooled to room temperature overnight and kept in a fridge for 5 days to complete crystallization. The crystals were again isolated manually and washed twice with anhydrous dichloromethane (0.20 ml). Yield: 15.35 mg = 14 %. MIR (ATR): (3500 – 3200 b, 3165 w, 3119 w, 1673 m, 1659 m, 1639 m, 1574 m, 1469 m, 1300 m, 1169 m, 1036 m, 939 s, 839 w) cm^{-1} . Elemental analysis for $\text{C}_{18}\text{H}_{17}\text{B}_3\text{LaN}_{15}\text{O}_6$ ($M_r = 710.80 \text{ g mol}^{-1}$): calcd. C 30.42; N 29.56; H 2.88 %; found: C 30.40; N 29.42; H 2.41 %.

Single crystal X-ray diffraction. Suitable single crystals of $[\text{La}(\text{NO}_3)_2\text{B}(\text{CN})_4(\text{H}_2\text{O})_4]$ (1) and $[\text{EMIM}]_\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (2) were selected from the crystalline products and mixed with high viscosity perfluorinated ether (99.9 %, ABCR). Data collection for both compounds was performed on a BRUKER AXS Apex II diffractometer at 100 K with a Helios-mirror using the BRUKER AXS Apex Suite program package.^[2] Continulative data processing was carried out using the XPREP package.^[3] Structure solutions were done with direct methods using SHELXT^[4] and refined with least-square techniques using SHELXL^[3] on the graphical platform OLEX2.^[5] For both compounds, all non-hydrogen atoms were refined anisotropically by least-square techniques, whereas the hydrogen atoms were fixed with geometrical constraints. Crystallographic data for both structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge, CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1532972 and 1532973. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>)

Powder X-ray diffraction. The samples (5 mg) for powder diffraction were placed on a zero-background silicon wafer. The diffraction data for all compounds were collected with a Bruker AXS D8 Discover Da Vinci powder X-ray diffractometer equipped with a Lynxx-Eye detector in reflection geometry. The X-ray radiation ($\text{Cu-K}_{\alpha 1}$; $\lambda = 154.06 \text{ pm}$) was focused with a Goebel mirror. The diffraction patterns were analyzed with the Bruker AXS Diffrac software suite. The lattice parameters of 1 and 2 were determined, and refined by Rietveld methods^[6] with the Bruker Topas Academic software.^[7]

IR- and Raman spectroscopy. IR spectra were recorded with a THERMO Nicolet 380 FT-IR spectrometer in transmission mode using OMNIC 32 software. Therefore, the compounds (5 mg) were investigated directly with an ATR unit. Raman spectra were measured on a Bruker IFS-120 spectrometer at room temperature using the 1064 nm excitation line of a Nd/YAG laser with an apodized resolution of 2 cm^{-1} on crystalline samples in melting point capillaries.

Elemental analysis. Carbon, nitrogen and hydrogen elemental analyses were conducted with a vario micro cube (Elementar Analysensysteme GmbH).

Crystallographic Data

Table S1: Crystallographic Data for $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**) and $[\text{EMIM}]\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (**2**).

	$\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (1)	$[\text{EMIM}]\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (2)
Formula	$\text{C}_4\text{H}_8\text{BLaN}_6\text{O}_{10}$	$\text{C}_{18}\text{H}_{17}\text{B}_3\text{LaN}_{15}\text{O}_6$
Fw / g·mol ⁻¹	449.88	710.80
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$
<i>a</i> / pm	1190.2(2)	956.1(2)
<i>b</i> / pm	1162.9(2)	2068.8(4)
<i>c</i> / pm	1085.0(2)	1648.7(3)
α / °	90	90
β / °	111.77(3)	104.85(3)
γ / °	90	90
<i>V</i> / 10 ⁶ pm ³	1394.7(6)	3152.2(12)
<i>Z</i>	4	4
ρ_{calc} / g·cm ⁻³	2.143	1.498
μ / cm ⁻¹	31.26	14.12
<i>F</i> (000)	864.0	1400.0
<i>T</i> / K	100	100
Data range	5.08 ≤ 2θ ≤ 55.99	3.23 ≤ 2θ ≤ 56.65
X-ray radiation	Mo-K α , λ = 71.07 pm	
Collected reflections	18300	48007
No. of unique reflections	3061	7852
<i>R</i> (int)	0.0315	0.0461
No. of parameters	203	414
<i>R</i> ₁ for reflections [<i>F</i> _o > 2σ(<i>F</i> _o)] ^[a]	0.0202	0.0302
<i>R</i> ₁ (all) ^[a]	0.0254	0.0392
<i>wR</i> ₂ (all) ^[b]	0.0460	0.0746
<i>S</i>	1.034	1.052
Res. electron density / e·10 ⁻⁶ pm ⁻³	0.81/−0.86	1.65/−1.13

a) $R_1 = \sum [|F_o| - |F_c|] / \sum |F_o|$. b) $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2] / \sum w(|F_o|^2)^2]^{1/2}$.

Table S2: Selected interatomic distances (pm) and angles (°) of $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**).

atom 1 – atom 2	distance / pm	atom 1 – atom 2 – atom 3	angle / °
La1 – N2	262.9(2)	N1 – La1 – N3 ^l	70.99(7)
La1 – N3 ^l	268.9(2)	N1 – La1 – O1	74.49(6)
La1 – O1	267.2(2)	O7 – La1 – N1	68.82(7)
La1 – O2	259.9(2)	O2 – La1 – O1	48.50(6)
La1 – O4	255.3(2)	O4 – La1 – O5	47.27(6)
La1 – O5	279.6(2)	O8 – La1 – O7	72.26(6)
La1 – O7	258.4(2)	O9 – La1 – O7	127.35(6)
La1 – O8	250.3(2)	O1 – N5 – O2	115.7(2)
La1 – O9	253.7(2)	O5 – N6 – O4	116.8(2)
La1 – O10	255.5(2)	C1 – B1 – C3	112.2(2)
B1 – C1	159.2(4)	C4 – B1 – C2	112.3(2)
B1 – C2	159.5(4)	N1 – C1 – B1	175.1(3)
C1 – N1	113.5(3)	N3 – C3 – B1	175.0(3)
C2 – N2	114.0(4)	N2 – C2 – B1	175.3(3)

l: x, ½ – y, –½ + z.

Table S3: Selected interatomic distances (pm) and angles (°) of [EMIM] $_{\infty}$ [LaNO₃{B(CN)₄}₃(H₂O)₃] (**2**).

atom 1 – atom 2	distance / pm	atom 1 – atom 2 – atom 3	angle / °
La1 – N1	271.1(2)	N4 ^{II} – La1 – N2	138.35(7)
La1 – N4 ^{II}	270.9(2)	N6 – La1 – N2	74.87(7)
La1 – N6	270.0(2)	N2 – La1 – N8 ^I	126.67(7)
La1 – N8 ^I	273.6(3)	N10 – La1 – N2	147.75(7)
La1 – N10	269.8(2)	O1 – La1 – O2	47.95(7)
La1 – O1	261.3(2)	O4 – La1 – O5	69.06(7)
La1 – O2	266.5(2)	O5 – La1 – O6	128.45(7)
La1 – O4	250.0(4)	O6 – La1 – N4 ^{II}	69.29(7)
La1 – O5	252.5(2)	O6 – La1 – N6	64.73(7)
La1 – O6	253.4(2)	O6 – La1 – N8 ^I	116.53(7)
B1 – C1	159.9(4)	O6 – La1 – N10	135.33(8)
B1 – C2	159.2(4)	N2 – C1 – B1	178.2(3)
B1 – C3	159.3(4)	N3 – C2 – B1	178.3(3)
B1 – C4	158.7(4)	N4 – C3 – B1	176.8(3)
C1 – N2	114.4(4)	N5 – C4 – B1	178.7(3)
C2 – N3	113.7(4)	C2 – B1 – C1	110.5(2)
C3 – N4	113.9(4)	C3 – B1 – C1	109.6(2)
C4 – N5	113.8(4)	C4 – B1 – C1	109.0(2)

I: 2-x, 1-y, 2-z; II: 1+x, y, z.

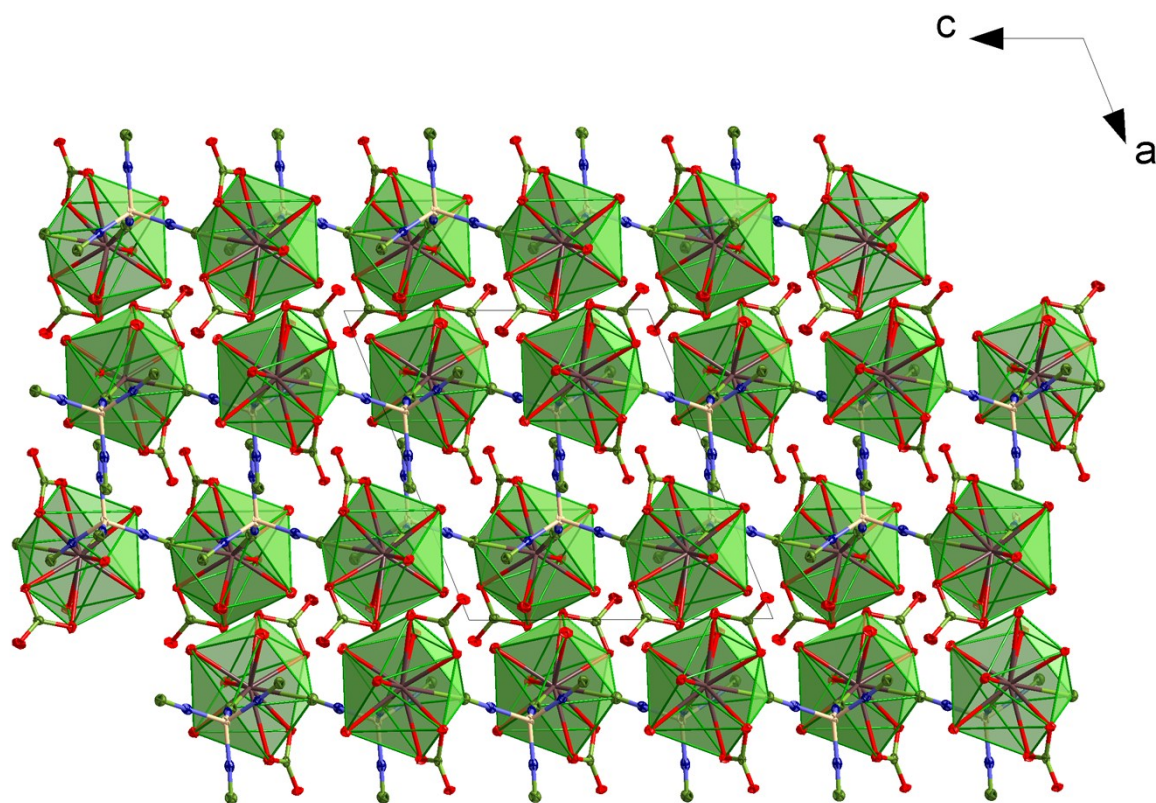


Fig. S1: Crystal structure of $_{\infty}$ [La(NO₃)₂[B(CN)₄](H₂O)₄] (**1**) with a view along the *b* axis; hydrogen atoms omitted for clarity.

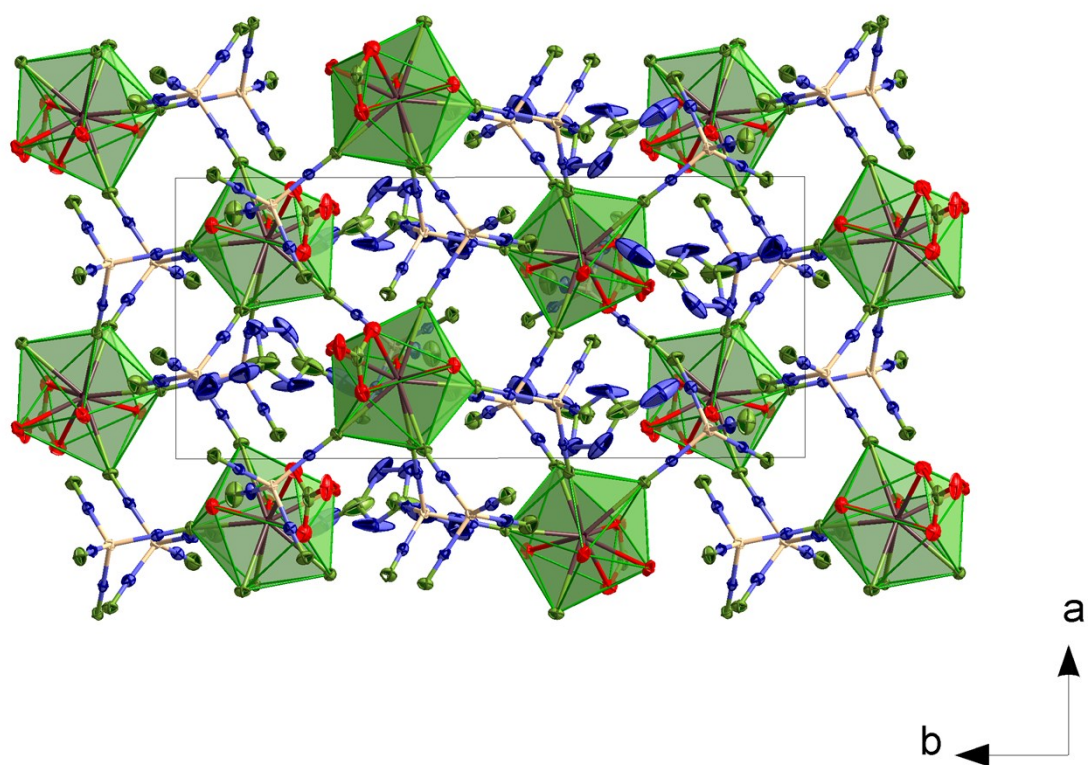


Fig. S2: Crystal structure of $[\text{EMIM}]_{\infty}[\text{LaNO}_3\{\text{B}(\text{CN})_4\}\{\text{H}_2\text{O}\}_3]$ (**2**) with a view along the *c* axis; hydrogen atoms omitted for clarity.

Powder X-ray diffraction

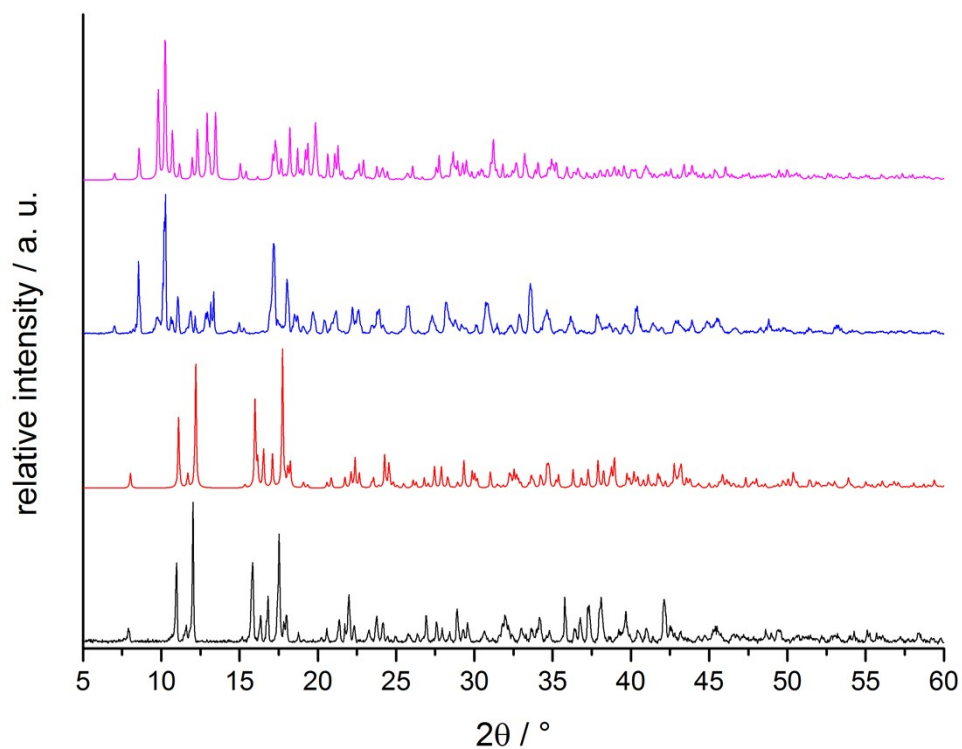


Fig. S3: Comparison of the observed X-ray powder diffraction patterns of $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**, black) and $[\text{EMIM}]\infty[\text{LaNO}_3[\text{B}(\text{CN})_4]_3(\text{H}_2\text{O})_3]$ (**2**, blue) with the powder patterns simulated from single-crystal data of **1** (red) and **2** (pink), respectively.

Table S4: Refined lattice parameters from the room-temperature X-ray powder data for $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**) and $[\text{EMIM}]\infty[\text{LaNO}_3[\text{B}(\text{CN})_4]_3(\text{H}_2\text{O})_3]$ (**2**).

Compound	La (1)	La (2)
Crystal System	monoclinic	
Space Group	$P2_1/c$	$P2_1/n$
a / pm	1206.3(2)	961.0(3)
b / pm	1172.3(5)	2069.7(8)
c / pm	1090.6(9)	1660.6(6)
β / °	112.14(5)	104.85(2)
$V/10^6 \text{ pm}^3$	1428.7(2)	3193.0(2)

IR-spectroscopy

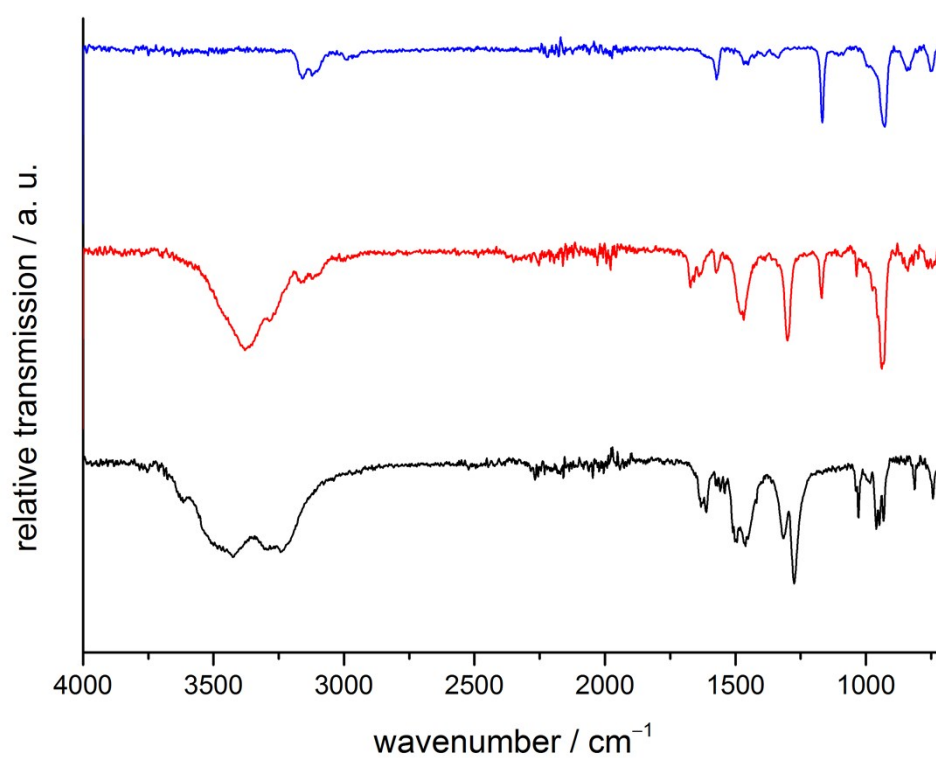


Fig. S4: IR spectra of the compounds $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**, black) and $[\text{EMIM}]_\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (**2**, red) as well as $[\text{EMIM}][\text{B}(\text{CN})_4]$ (blue).

Raman-spectroscopy

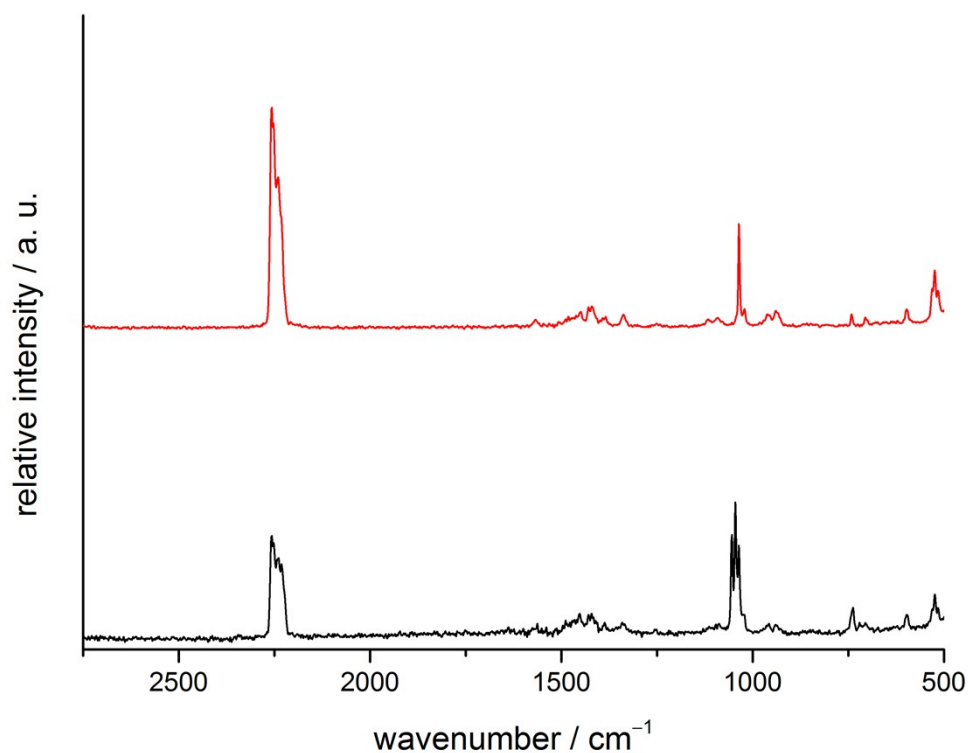


Fig. S5: Raman spectra of the compounds $\infty[\text{La}(\text{NO}_3)_2[\text{B}(\text{CN})_4](\text{H}_2\text{O})_4]$ (**1**, black) and $[\text{EMIM}]\infty[\text{LaNO}_3\{\text{B}(\text{CN})_4\}_3(\text{H}_2\text{O})_3]$ (**2**, red).

Supporting Information References

- [1]: U. Welz-Biermann, N. Ignatyev, E. Bernhardt, M. Finze, H. Willner, Salts comprising cyanoborate anions, Merck Patent GmbH, WO2004072089, 2004.
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