

Unexpected Dimeric Spiro-Borate Complexes from Lewis-Acid Induced Transformation of Oxalatoborates

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Dedicated to Professor Johannes Beck on the Occasion of His 60th Birthday

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Abstract. Oxalatoborates were transformed into dimeric spiro-borate complexes by abstraction of oxalate ligands by Lewis acidic lanthanide trichlorides. Oxalatoborates with different anions and cations were investigated containing either bis-oxalatoborate or catecholato-oxalatoborate anions and lithium as well as EMIM (1-ethyl-3-methyl-imidazolium) and BMIM cations (1-n-butyl-3-methyl-imidazolium) from the respective ionic liquids (ILs). Depending on the amount of oxalate groups and the different cations, the oxalate groups are partly or fully abstracted and transferred to the lanthanides. The reaction of anhydrous PrCl₃ with Li[B(C₆H₄O₂)(C₂O₄)] (lithium catecholato-oxalatoborate = Li[Catbox]) in pyridine (py) led to a conversion of the borate anion to the complex [B₂O(C₆H₄O₂)(py)₄][PrCl₅(py)] (1). The use of

Introduction

Lithium bis-oxalatoborate (Li[BOB]) is currently under investigation as electrolyte component for Li-ion batteries,^[1] because lithium borates are considered for high-temperature operations due to their thermal stability.^[2] Besides common lithium salts such as Li[PF₆] or LiClO₄ a whole set of lithium borates including Li[BF₄] or Li[B(C₂O₄)₂] (Li[BOB]) was examined as potential electrolyte constituents.^[2]

Although Li[BOB] is well explored concerning its electrochemical behavior^[3] and thermal properties,^[4] there is limited knowledge about its behavior in coordination chemistry, besides its crystal structure, and some solvates of Li[BOB] such as Li[BOB]·H₂O.^[5] Li[BOB] was further used to synthesize the ionic liquid 1-ethyl-3-methylimidazolium bis-oxalatoborate [EMIM][BOB], which could be utilized for the ionothermal synthesis of novel manganese and cobalt borophosphates.^[6]

the ILs [EMIM][Catbox] and [BMIM][Catbox] indicates complete transfer of the oxalate groups to the lanthanide ions in reactions with lanthanide chlorides and nitrates yielding the well-known lanthanide oxalates $Ln_2(C_2O_4)_3$ ·10H₂O (Ln = La, Eu). In contrast, the reaction of anhydrous YCl_3 with $Li[B(C_2O_4)_2]$ (lithium bis-oxalatoborate = Li[BOB]) in N,N-dimethylformamide (dmf) results in the formation of $[B_2O(C_2O_4)_2(dmf)_2]$ (2). Transfer of one oxalate group per boron onto the yttrium ion is revealed by the formation of the one-dimensional coordination polymer ${}^{1}_{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (3) as additional product. The products were characterized by single-crystal X-ray diffraction as well as powder X-ray diffraction, IR spectroscopy and elemental analysis.

Closely related to Li[BOB] is Li[B($C_6H_4O_2$)(C_2O_4)] (lithium catecholato-oxalatoborate = Li[Catbox]), which was also investigated regarding its electronic properties and hence its possible use as electrolyte component for Li-ion batteries.^[7] As both of these lithium salts may be suitable for the formation of coordination compounds due to their oxalate groups, they might also be interesting in widening the knowledge on novel organoborates. In the light of a large number of known inorganic lanthanide oxo-borates,^[8] there is rather little known about oxoborate anions as functional ligands for lanthanide coordination compounds. Some examples were described with a coordination of the tetra-methoxyborate anion in $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]^{[9]}$ (Ln = La, Pr, Nd), and $[\{Na\}\{(sal)_3Ln(B(OCH_3)_4)Ln(sal)_3\}]_n^{[10]}$ (sal = salicylato and Ln = Y, Nd, Eu – Lu). Recently, some structural insights borate)₃ $Ln(thf)_3$]•thf^[11] (Ln = Nd, Sm; thf = tetrahydrofurane), as well as the coordination polymer $\frac{1}{\infty}[Pr(BSB)_3(py)_2]^{[12]}$ (BSB = bis(salicylato)borate and py = pyridine).

The intention of the work presented herein was to investigate the suitability of the bis-oxalatoborate and catecholatooxalatoborate anion as potential ligands for lanthanide coordination compounds under solvothermal as well as ionothermal conditions. However, it resulted in the formation of unexpected dimeric spiro-borate complexes.

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Results and Discussion

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General Considerations

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For reactions of oxalatoborates with lanthanides, several different precursors were investigated in this work: Both, bisoxalatoborate and catecholato-oxalatoborate anions together with Li, EMIM and BMIM cations were reacted with trichlorides and nitrates of several different lanthanides. No direct coordination of the lanthanide cations to oxoborate groups could be observed, but abstraction of complete oxalate anions. The complex $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1) was obtained from Li-catecholato-oxalatoborate Li[Catbox] and anhydrous PrCl₃ in pyridine (py) at 110 °C, indicating transfer of the oxalate group on the boron, while retaining the catecholate group. Further investigations with the ILs [EMIM][Catbox] and [BMIM][Catbox] (EMIM = 1-ethyl-3-methyl-imidazolium; BMIM = 1-*n*-butyl-3-methyl-imidazolium) with both, La(NO₃)₃·6H₂O and EuCl₃·6H₂O, corroborates the transfer of the oxalate groups to the lanthanides yielding solid crystalline products that could be identified as $La_2(C_2O_4)_3 \cdot 10 H_2O$ and Eu₂(C₂O₄)₃·10 H₂O.^[13] Utilization of bis-oxalatoborates leads to the abstraction of just one oxalate group while retaining the other on the boron. $[B_2O(C_2O_4)_2(dmf)_2]$ (2) and $\frac{1}{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (**3**) were obtained by reaction of YCl₃ with Li[BOB] in N.N-dimethylformamide (dmf) in sealed ampoules. The formation of both reaction products is temperature dependent with $[B_2O(C_2O_4)_2(dmf)_2]$ (2) being formed as single crystals at 80 °C already, followed by the emergence of ${}^{1}_{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (**3**) as bulk product from 85° to

120 °C. These findings are supported by previously reported experimental and theoretical studies that deal with possible conversion products of Li[BOB].^[14] However, the formation of *spiro*-borate complexes, as reported herein, is quite unexpected.

Crystal Structures

Crystal Structure of $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1)

The compound $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1) crystallizes in the orthorhombic crystal system in the space group *Pbca*. Crystallographic data are presented in Table 1 and selected interatomic distances are given in Table S1 (Supporting Information). The spiro-borate complex is a cation, boron atoms are μ -connected by an oxygen atom and exhibit a tetrahedron as coordination polyhedron (Figure 1). The tetrahedron is formed by two oxygen atoms and two nitrogen atoms, respectively. The nitrogen atoms originate from py, oxygen from the catecholate group and linking oxygen atom.

The B-O distances are in a range of 139.9(5)-142.6(5) pm and good agreement with B-O in in $[Ph_3PNPPh_3][B_2O(C_6H_4O_2)_2(OAc)]$ (137.5–161.7 pm)^[15] and $[C_6H_{11}N_2][B_5H_4O_{10}]$ (135.7–147.4 pm).^[16] The B–N distances are from 161.2(6) to 163.1(6) pm and consistent with related B–N distances in $C_{32}H_{34}B_2N_2O_4$ (161.6 pm)^[17] and C₃₄H₃₈B₂N₂O₂ (159.0–163.6 pm).^[18] The structural motif of two µ-connected boron atoms coordinated by two oxygen atoms and two nitrogen atoms is known, e.g. from C₃₄H₃₂B₂N₄O₅, but nevertheless quite rare.^[17,19]

Table 1. Crystallographic data for $[B_2O(C_6H_4O_2)(py)_4]$ [PrCl₅(py)] (1), $[B_2O(C_2O_4)_2(dmf)_2]$ (2), and $\frac{1}{2}$ [LiYCl₂(C₂O₄)(dmf)₃] (3).

	$[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1)	$[B_2O(C_2O_4)_2(dmf)_2]$ (2)	${}^{1}_{\infty}$ [LiYCl ₂ (C ₂ O ₄)(dmf) ₃] (3)
Formula	C ₃₁ H ₂₉ B ₂ Cl ₅ N ₅ O ₃ Pr	C ₁₀ H ₁₄ B ₂ N ₂ O ₁₁	C ₁₁ H ₂₁ LiYCl ₂ N ₃ O ₇
Fw /g·mol ⁻¹	859.37	359.85	474.06
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_{1}/c$	$P2_1/n$
a /pm	1615.6(4)	806.2(2)	1128.2(2)
<i>b</i> /pm	2079.1(1)	1214.4(2)	1788.3(4)
c /pm	2130.7(6)	1574.4(3)	1137.3(2)
$a /^{\circ}$	90	90	90
β /°	90	96.04(3)	119.40(3)
γ /°	90	90	90
V /10 ⁶ pm ³	7157.2(7)	1532.8(5)	1999.0(9)
Ζ	8	4	4
$\rho_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	1.595	1.559	1.575
μ /cm ⁻¹	17.75	1.39	32.18
F(000)	3424	744.0	960.0
Т /К	100(2)	100(2)	100(2)
Data range	$3.72 \le 2\Theta \le 60.24^{\circ}$	$4.24 \le 2\Theta \le 56.90^{\circ}$	$4.16 \le 2\Theta \le 56.66^{\circ}$
X-ray radiation		Mo- K_{α} , $\lambda = 71.07 \text{ pm}$	
Collected reflections	107563	17979	25068
No. of unique reflections	10191	3829	4951
<i>R</i> (int)	0.1137	0.0824	0.0417
No of parameters	470	282	224
R_1 for reflections $[F_0 > 2\sigma (F_0)]^{a}$	0.0441	0.0594	0.0382
R_1 (all) ^{a)}	0.0988	0.1156	0.0518
wR_2 (all) ^{b)}	0.1121	0.1475	0.0965
S	0.995	1.024	1.127
Res. electron density /e•10 ⁻⁶ pm ⁻³	1.28/-1.17	0.37/-0.29	0.67/-0.58

a) $R_1 = \sum [|F_0| - |F_c|] / \sum |F_0|$. b) $wR_2 = [\sum w (|F_0|^2 - |F_c|^2)^2] / \sum w (|F_0|^2)^2]^{1/2}$.^[20]





Figure 1. Coordination sphere of the spiro-borate cations of $[B_2O(C_6H_4O_2)(py)_4]^{2+}$ in **1** (top) and of the praseodymium atom in the anion $[PrCl_5(py)]^{2-}$ (center). Crystal structure of **1** with polyhedra along the *a* axis (bottom); hydrogen atoms and aromatic rings are omitted for clarity. All depictions in this and all following figures show thermal ellipsoids depicting 50 % of the probability level of the atoms.

The complex lanthanide anion shows an octahedron as coordination polyhedron for Pr^{3+} that is formed by five chloride ligands and one pyridine molecule. The Pr–Cl distances are in a range of 270.98(11)–276.66(9) pm and in good agreement

with Pr–Cl distances in related compounds such as $[C_6H_{11}N_2]_3[PrCl_6]$ (Pr–Cl: 272.2–276.3 pm)^[21] or $[Pr_2Cl_6(bipy)(py)_6]$ (bipy = 4,4'-bipyridine, Pr–Cl: 269.3–273.0 pm).^[22] The Pr–N distance of 266.2(3) pm is also in good accordance with Pr–N distances found in the literature, e.g. in ${}^{2}_{\infty}[Pr_2Cl_6(bipy)_3]$ -2bipy (Pr–N: 261.5–266.9 pm)^[23] and $[Pr_2Cl_6(bipy)(py)_6]$ (Pr–N: 263.7–267.3 pm).^[22] The anions are located on the *ac* plane in the crystal structure, whereas the cations are positioned so that the tetrahedrally coordinated boron atoms occupy a bisecting line of the *ab* plane.

Crystal Structure of $[B_2O(C_2O_4)_2(dmf)_2]$ (2)

The complex $[B_2O(C_2O_4)_2(dmf)_2]$ (2) crystallizes in the monoclinic crystal system in the space group $P2_1/c$. Crystallographic data are presented in Table 1 and selected interatomic distances are given in Table S2 (Supporting Information). The



Figure 2. Coordination sphere of the boron atoms in $[B_2O(C_2O_4)_2(dmf)_2]$ (2) (top) and crystal structure of 2 along the *a* axis (bottom).

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two crystallographically independent boron atoms are both coordinated by four oxygen atoms exhibiting a tetrahedron as coordination polyhedron (Figure 2). The boron atoms are µconnected by an oxygen atom and both are further coordinated by one dmf molecule and one oxalate ion. Different from 1, the spiro-borate complex is neutral and does not require a counteranion. The B-O distances are in a range of 138.7(3)-151.0(3) pm being in good agreement with B-O distances in $[Ph_3PNPPh_3][B_2O(C_6H_4O_2)_2(OAc)]$ (B-O: 137.5-161.7 pm) ^[15] and $[C_6H_{11}N_2][B_5H_4O_{10}]$ (B–O: 135.7–147.4 pm).^[16]

Crystal Structure of ${}^{1}_{\infty}[LiYCl_{2}(C_{2}O_{4})(dmf)_{3}]$ (3)

The strand-like coordination polymer ${}^{1}_{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (3) crystallizes in the monoclinic crystal system in the space group $P2_1/n$. Crystallographic data are presented in Table 1, also, and selected interatomic distances are given in Table S3 (Supporting Information). The Y³⁺ ion exhibits a pentagonalbipyramid as coordination polyhedron that is constituted by five oxygen atoms in an equatorial plane and two chlorine atoms occupying the axial positions within the bipyramid (Figure 3). The Li⁺ ion is coordinated tetrahedrally by four oxygen atoms, two of them belonging to coordinating dmf-molecules. Both polyhedra are linked via a shared edge, which is built by two oxygen atoms. The interatomic Y-Cl distances of 260.03(10) and 261.20(10) pm are in good agreement with Y-Cl distances found, e.g. for [YCl₃(py)₄] (Y-Cl: 258.74-263.88 pm)^[24] and [YCl₂(Ph₃PO)₄]Cl·2.5EtOH·H₂O (Y–Cl: 261.3-262.5 pm).^[25] The Y-O distances are in a range of 225.3(2)-237.6(2) pm and show good accordance with Y-O distances in K₈[Y₂(C₂O₄)₇]·14H₂O (Y-O: 229.9-238.6 pm)^[26] and [YCl₂(thf)₅][YCl₄(thf)₂] (Y-O: 229.3-239.1 pm).^[27] For Li-O different distances are observed in a range of 187.5(6)-199.5(6) pm that is typical for a tetrahedral coordination sphere around Li⁺ ions (Li-O: 185-200 pm).^[28] The coordination polyhedra of the yttrium atoms are connected by two edges formed by two oxygen atoms of the oxalate unit, thus resulting in an one-dimensional coordination polymer. As these oxalate groups are twisted alternately by 90°, the coordination polyhedra are also rotated by 90° in the chain, respectively. The onedimensional strands are also stacked in the unit cell with a rotation of 90° for each subsequent strand.

PXRD Investigations

The powder X-ray diffraction pattern of the bulk product of $\frac{1}{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (**3**) shows good accordance with a diffraction pattern simulated from single crystal data of 3, thus proving the phase purity of the obtained bulk material (Figure 4).

Furthermore, the solid reaction products of the reactions of La(NO₃)₃·6H₂O with [BMIM][Catbox] and EuCl₃·6H₂O with [EMIM][Catbox] could be identified with powder X-ray diffraction as $La_2(C_2O_4)_3$ ·10H₂O and $Eu_2(C_2O_4)_3$ ·10H₂O, respectively.^[13] These findings also show that the borate anions undergo a transformation during the reactions by transferring the oxalate group of the [Catbox]⁻ anions to the lanthanide ions,



Figure 3. Extended Y³⁺ and Li⁺ coordination spheres in ${}_{\infty}^{1}$ [LiYCl₂(C₂O₄)(dmf)₃] (3). Symmetry operation: 1-x, -y, 1-z (top). One-dimensional chain-excerpt of 3 (center). Crystal structure of 3 along the *a* axis (bottom).



Figure 4. Observed and simulated diffraction patterns of ${}_{a}^{1}$ [LiYCl₂(C₂O₄)(dmf)₃] (**3**) as well as comparison of the observed patterns of La₂(C₂O₄)₃·10H₂O and Eu₂(C₂O₄)₃·10H₂O that were obtained from the reactions of EuCl₃·6H₂O with [EMIM][Catbox] and of La(NO₃)₃·6H₂O with [BMIM][Catbox], respectively. In addition, the ideal reflection positions and simulated intensities of La₂(C₂O₄)₃·10H₂O are given (top).^[13] IR spectra of ${}_{a}^{1}$ [LiYCl₂(C₂O₄)(dmf)₃] (**3**) and [B₂O(C₆H₄O₂)(py)₄][PrCl₅(py)] (**1**) (bottom).

thereby promoting the formation of lanthanide oxalates, which are obviously favored products.

Vibrational Spectroscopy

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The obtained compounds $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1) and $\frac{1}{\infty}[LiYCl_2(C_2O_4)(dmf)_3]$ (3) were investigated by IR spectroscopy (Figure 4). The sharp bands at 1805 and 1772 cm⁻¹ in the IR spectrum of $\frac{1}{\infty}[[LiYCl_2(C_2O_4)(dmf)_3]$ (3) can be assigned to the stretching vibrations C=O of the oxalate groups, whereas the strong band at 1641 cm⁻¹ can be identified as the C=O stretching vibration of the dmf-molecules that coordinate to the Y³⁺ and Li⁺ ions. Consistent with these findings are the bands at 1442 and 1380 cm⁻¹ that can be explained by the C–H bending vibrations of the dmf molecules. Furthermore, the bands at 1303, 1218, and 1143 cm⁻¹ can be attributed to the stretching vibrations of the O–C–O-skeleton in the oxalate groups.

Considering the IR spectrum of $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1), the stretching vibrations of the coordinating pyridine molecules can be observed at 3063 (C-H) and 1624 (C=C) cm⁻¹, whereas the vibrations of the aromatic ring can be found at 1485, 1462, and 1439 cm⁻¹. The stretching vibrations of the C=O groups appear at 1794 and 1751 cm⁻¹ and are slightly shifted and of lower intensity compared to free Li[Catbox]. The band at 1535 cm⁻¹ can be assigned to the B-N stretching vibration,^[29] whereas the bands at 1315 and 1234 cm⁻¹ can be explained by the stretching vibrations of the B-O-C units in (1).[30] $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ Moreover, the bands at 1149, 1099, and 1065 cm⁻¹ can be interpreted as stretching vibrations of the B-O-B units in $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1).

The solid *Ln*-oxalate products of the reactions of EuCl₃·6H₂O with [EMIM][Catbox] and of La(NO₃)₃·6H₂O with [BMIM][Catbox] were also examined via IR spectroscopy. The IR spectra of both products show intense bands at 1602 cm⁻¹ that are characteristic for the C=O stretching modes in oxalates, thus giving further evidence for the formation of the oxalates La₂(C₂O₄)₃·10H₂O and Eu₂(C₂O₄)₃·10H₂O^[13] (see Figure S1, Supporting Information).

Conclusions

Unexpected dimeric spiro-borate complexes were obtained from oxalatoborates by abstraction of oxalate ligands with Lewis acidic lanthanide trichlorides. Thereby, the constitution of the oxalatoborates distinguishes the amount of oxalato groups that are transferred onto the lanthanide ions. Bis-oxalatoborate or catecholato-oxalatoborate anions were investigated together with lithium as well as EMIM and BMIM cations as ionic liquids. No direct coordination of oxoborate groups to lanthanide cations was observed. The reaction of Li[Catbox] and PrCl₃ in pyridine yields $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ with a rare structural motif, as boron is coordinated by two oxygen and two nitrogen atoms in the spiro complex, whereas the lanthanide content is found in the counteranion. The formation of lanthanide oxalates drives the oxalate abstraction and could be proven e.g. for the ionic liquids [EMIM][Catbox] and [BMIM][Catbox] yielding $Ln_2(C_2O_4)_3$ ·10H₂O. Aside from pure oxalates, also mixed ligand species are possible abstraction products: The reaction of YCl₃ with Li[BOB] in dmf revealed the formation of the one-dimensional coordination polymer $\frac{1}{\infty}$ [LiYCl₂C₂O₄(dmf)₃]. For bis-oxalatoborates, the respective spiro-borate complex was found to have the constitution $[B_2O(C_2O_4)_2(dmf)_2]$ retaining one oxalate group instead of a catecholate.

Experimental Section

All manipulations except for the reactions with the ionic liquids [EMIM][Catbox] and [BMIM][Catbox] were carried out under inert conditions using vacuum line, Schlenk, glovebox (MBraun, Labmaster SP, and Innovative Technology, Pure Lab) and Duran[®] glass ampoule techniques. For a controlled heating of the sealed glass ampoules, heating furnaces based on Al₂O₃ tubes with Kanthal wire resistance and

NiCr/Ni temperature elements regulated by Eurotherm 2416 control units were utilized. The used starting materials YCl₃ (99.9%, Strem Chemicals), PrCl₃ (99.9%, Strem Chemicals), EuCl₃·6H₂O (99.9%, Chempur) and La(NO₃)·6H₂O (99.0%, Merck) were used as purchased. Anhydrous pyridine (99.5%, Alfa Aesar) and anhydrous *N*,*N*-dimethylformamide (99.9%, Alfa Aesar) were stored over molecular sieve. LiB(C₂O₄)₂ (Li[BOB], 99.0%, Chemetall) was used as purchased, whereas Li[Catbox], EMIM[Catbox] and BMIM[Catbox] were synthesized as described elsewhere.^[31] The respective reagents were sealed into evacuated (1×10^{-3} mbar) glass ampoules and further treated as described below.

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Synthesis of [B₂O(C₆H₄O₂)(py)₄][PrCl₅(py)] (1): PrCl₃ (0.12 mmol, 29.7 mg), Li[Catbox] (0.2 mmol, 80.9 mg), and pyridine (0.1 mL) were mixed, transferred into an ampoule and heated to 110 °C in 17 h. This temperature was maintained for 12 h until a few green crystals had formed in the heat. The ampoule was cooled down to room temperature in 28 h and the crystals were isolated manually, washed with pyridine (2 × 0.1 mL), and dried in vacuo. MIR (ATR): $\tilde{v} = 3428$ b, 3063 m, 2962 w, 2920 w, 1794 w, 1751 m, 1624 s, 1535 m, 1485 s, 1462 s, 1439 s, 1315 m, 1234 s, 1149 w, 1099 m, 1065 m, 910 m, 791 m, 748 m, 702 m, 679 m, 609 w cm⁻¹. C₃₁H₂₉B₂Cl₅N₅O₃Pr (M_r = 859.37 g·mol⁻¹): calcd. C 43.33; N 8.15; H 3.40%; found: C 44.34; N 6.64; H 2.94 %.

Synthesis of $[B_2O(C_2O_4)_2(dmf)_2]$ (2): YCl₃ (0.2 mmol, 39.1 mg), Li[BOB] (0.4 mmol, 77.5 mg), and dmf (0.1 mL) were mixed, filled into an ampoule and heated to 80 °C in 24 h. This temperature was maintained for 72 h before cooling down to room temperature in 2 h. A few colorless crystals formed in the heat and could be isolated manually. C₁₀H₁₄B₂N₂O₁₁ (M_r = 359.85 g·mol⁻¹): calcd. C 33.38; N 7.78; H 3.92 %; found: C 32.07; N 8.93; H 3.37 %.

Synthesis of ${}^{1}_{\infty}$ [LiYCl₂(C₂O₄)(dmf)₃] (3): YCl₃ (0.2 mmol, 39.1 mg), Li[BOB] (0.4 mmol, 77.5 mg), and dmf (0.1 mL) were mixed and filled into an ampoule and heated to 120 °C in 10 h. This temperature was maintained for 48 h before cooling down to room temperature in 30 h. The reaction product was washed with anhydrous dmf (3 × 0.1 mL) and dried in vacuo. The reaction yielded needle-shaped, colorless crystals and microcrystalline powder. Yield: 72 mg, 76%. **MIR** (ATR): $\tilde{v} = 1805$ s, 1772 s, 1641 s, 1442 m, 1380 s, 1303 m, 1218 m, 1143 m, 1083 s, 985 m, 811 w, 784 w cm⁻¹. C₁₁H₂₁Cl₂LiYN₃O₇ (Mr = 474.06 g·mol⁻¹): calcd. C 27.81; N 7.74; H 4.46%; found: C 28.72; N 8.04; H 4.06%.

Single Crystal X-ray Diffraction: Suitable single crystals of $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1), $[B_2O(C_2O_4)_2(dmf)_2]$ (2) and ${}^{1}_{\infty}$ [LiYCl₂C₂O₄(dmf)₃] (**3**) were selected for X-ray diffraction from the crystalline products deposited above the mother-liquor by subsequent mixing with high viscosity perfluorinated ether (99.9%, ABCR). Data collection for all 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.[32] Data processing was accomplished with XPREP.^[20] All structure solutions were carried out with direct methods using SHELXT^[33] and the obtained crystal structures were refined with least square techniques using SHELXL^[20] on the graphical platform OLEX2.^[34] For all compounds, the nonhydrogen atoms were refined anisotropically by least square techniques, whereas all hydrogen atoms were fixed with geometrical constraints. Moreover, a systematic displacement of a coordinating pyridine molecule in the cation of $[B_2O(C_6H_4O_2)(py)_4][PrCl_5(py)]$ (1) was refined.

Crystallographic data (excluding structure factors) for the structures 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-1499781, CCDC-1499782, and CCDC-1499783. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk)

Powder X-ray Diffraction; Samples for powder diffraction were grinded in a mortar and put into Lindemann glass capillaries (Ø 0.5 mm). Diffraction data was measured with a powder X-ray diffractometer BRUKER AXS D8 Discover provided with a Lynxx-Eye detector in transmission geometry. X-ray radiation (Cu- K_{a1} ; $\lambda = 154.06$ pm) was focused with a Goebel mirror, whereas Cu- K_{a2} radiation was eliminated by use of a Ni absorber. Diffraction patterns were collected and analysed using the BRUKER AXS Diffrac-Suite.

Vibrational Spectroscopy: IR spectra were measured with a THERMO Nicolet 380 FT-IR spectrometer in transmission mode using OMNIC 32 software. Therefore, the compounds (5 mg) were mixed with anhydrous KBr (300 mg) and pressed to transparent pellets or an ATR unit was used.

Elemental Analysis: Carbon, nitrogen and hydrogen elemental analysis was carried out with a vario micro cube (Elementar Analysensysteme GmbH).

Supporting Information (see footnote on the first page of this article): Selected interatomic distances and angles for compounds 1–3, additional IR spectroscopic investigations, additional crystal structure figures and experimental on the oxalate splitting from ILs.

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Unexpected Dimeric Spiro-Borate Complexes from Lewis-Acid Induced Transformation of Oxalatoborates

