

First blue luminescent diborate compound: $B_2(\mu-O)Et_2(7\text{-azain})_2$ (7-azain = 7-azaindole anion)

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A novel blue luminescent diborate compound $B_2(\mu-O)Et_2(7\text{-azain})_2$ (7-azain = 7-azaindole anion) is synthesized and characterized structurally; it emits a blue color at $\lambda_{\text{max}} = 422$ nm in the solid and at $\lambda_{\text{max}} = 419$ nm in solution and is stable under air as a solid.

Blue luminescent compounds are among the most sought-after materials by scientists in both academia and industry because of their potential applications in electroluminescence displays.¹ Most of the previously reported blue luminescent compounds in electroluminescent displays are either aromatic organic molecules or organic polymers.¹ Blue luminescent inorganic and organometallic complexes are rather rare and have been limited to 8-quinoline or azomethine based complexes where either Al or Zn ions are involved.² During our investigation of alkylaluminum amido and imido chemistry, we have discovered two families of blue luminescent aluminium complexes based on either the deprotonated di-2-pyridyl amine ligand or 7-azaindole ligand.³ Both di-2-pyridyl amine (Hdpa) and 7-azaindole (7-Hazain) have no visible blue luminescence under UV radiation at ambient temperature. Upon reaction with $AlMe_3$, these two ligands produce a variety of blue luminescent aluminium complexes.⁴ One weakness associated with these aluminium compounds is their tendency to undergo hydrolysis upon exposure to air. Although we have found that the incorporation of alkoxo and oxo ligands into the complexes enhances their thermal and air stability without destroying the blue luminescence,⁴ they are, however, still vulnerable, to some extent, to air and moisture. In contrast to organoaluminium compounds, organoboron compounds are in general more stable owing to the increased covalency of B–C and B–N bonds,⁵ in comparison to those of Al–C and Al–N bonds. We therefore explored the synthesis of boron compounds containing either the di-2-pyridylamine or the 7-azaindole ligand. We report here the first example of a blue luminescent diborate compound, $B_2(\mu-O)Et_2(7\text{-azain})_2$ **1**.

The colorless diborate compound was isolated in *ca.* 30% yield from the reaction of BEt_3 with 7-azaindole and 1,1,1,3,3,3-hexafluoropropan-2-ol in a 2 : 2 : 1 ratio in toluene at 25 °C. This compound can also be obtained by the reaction of BEt_3 with 7-azaindole and water in a 2 : 2 : 1 ratio in *ca.* 10% yield. The role played by 1,1,1,3,3,3-hexafluoropropan-2-ol in the synthesis has not, as yet, been understood. ¹H NMR spectroscopy, single-crystal X-ray diffraction and elemental analyses† established the formula of this compound to be $B_2(\mu-O)Et_2(7\text{-azain})_2$ **1**. The crystal structure along with important bond lengths and angles are given in Fig. 1. Compound **1** contains two B atoms in a tetrahedral environment. The 7-azaindole ligand is bound to the B centers *via* both N atoms. Both 7-azaindole ligands are disordered with 50% occupancy for each of the disordered sites. Consequently, the B–N bond lengths are the average of B–N(indole) and B–N(pyridyl) bonds, ranging from 1.604(5) to 1.612(5) Å, which are consistent with the typical B–N bond lengths reported previously.^{6,7} Each B is also bound by an ethyl group with a normal B–C bond length. The most interesting structural feature of this molecule is the bridging O atom which can be considered as the consequence of the reaction of two ethyl groups with one water

molecule. A similar oxygen bridge has been observed in the compound $B_4(2,2'\text{-biimidazole})_2(O)Et_6$ reported by Niedenzu *et al.*^{6a} The B–O bond lengths in compound **1** are typical^{6,7} and similar to those found in Niedenzu's compound. The B–O–B angle [151(3)°] in Niedenzu's compound is, however, much larger than that in compound **1** [119.6(3)°] which can be attributed to the different steric strain imposed by the 2,2'-biimidazole and the 7-azaindole ligands. As a result of the bridging oxygen atom, compound **1** has a bicyclo[3.3.1]nonane-like structure. Similar B–O–B bridges have also been observed previously in heterocycles of boric or boronic acids or their acyloxy or acylamino derivatives based on the bicyclo[3.3.1]nonane framework.⁷ To our knowledge, compound **1** is the first example of biheterocycles involving 7-azaindole, boron and oxygen atoms.

The most exciting property of **1** is that it emits an intense blue color upon irradiation by UV light. The emission maximum in the solid is at $\lambda = 422$ nm. The free 7-azaindole does not have any observable blue luminescence in the solid state. The toluene solution of compound **1** emits at $\lambda_{\text{max}} = 419$ nm at 23 °C while the toluene solution of the free 7-azaindole ligand has an emission band at $\lambda_{\text{max}} = 357$ nm which is in the colorless UV region. In addition to the dramatic shift of the emission band, the relative emission intensity† of compound **1** in solution also appeared to be much greater than that of the free ligand (Fig. 2). The role of the boron atom in the blue luminescence of **1** was therefore considered to be perhaps twofold. First, the formation of covalent bonds between the B and N atoms *via* the donation of lone-pairs of the N atoms to the B atoms changes the emission energy from UV to blue, perhaps owing to the lowering of the energy gap between π^* and π . Second, the

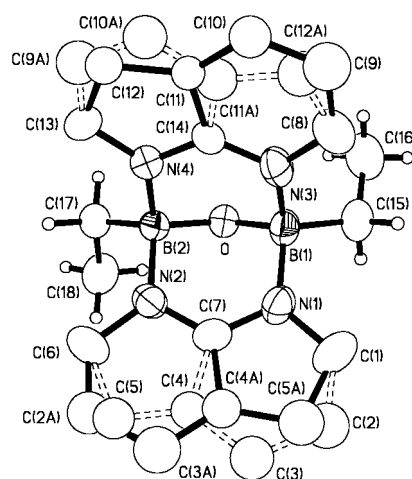


Fig. 1 The molecular structure of compound **1** with 50% thermal ellipsoids and labelling scheme. The second set of positions of the disordered 7-azaindole ligands are shown as dashed lines. Important bond lengths (Å) and angles (°): B(1)–O 1.430(5), B(1)–N(1) 1.604(5), B(1)–N(3) 1.609(5), B(1)–C(15) 1.595(6), B(2)–O 1.431(5), B(2)–N(2) 1.612(5), B(2)–N(4) 1.604(5), B(2)–C(17) 1.592(5); B(1)–O–B(2) 119.6(3), N(1)–B(1)–N(3) 104.6(3), O–B(1)–C(15) 115.9(4), N(2)–B(2)–N(4) 105.2(3), O–B(2)–C(17) 115.9(3)°.

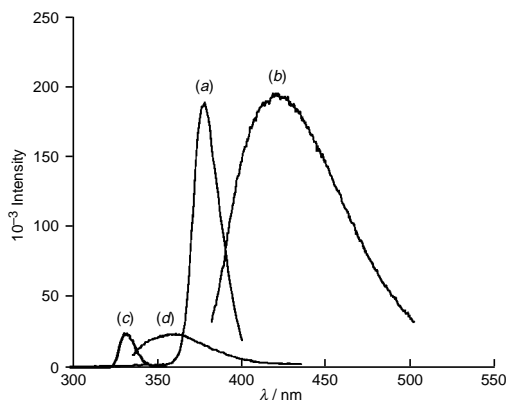


Fig. 2 Excitation and emission spectra of **1** and 7-azaindole in solution at 23 °C: (a) and (b) are the excitation and emission spectra of compound **1** (6.75×10^{-3} M in toluene); (c) and (d) are the excitation and emission spectra of 7-azaindole (3.67×10^{-2} M in toluene)

binding of the 7-azaindole ligand to two B atoms increases the rigidity of the ligand, thus reducing the loss of energy *via* vibrational motions and increasing the emission efficiency,^{8a} a phenomenon well known to coordination compounds containing luminescent chelating ligands.^{8b,c} However, our attempt to measure the quantum yields of the free ligand and the boron compound against a common reference compound was unsuccessful because they absorb at different regions. The emission quantum yield of compound **1** was determined to be 0.47, relative to that of 9,10-diphenylanthracene while the quantum yield of the free ligand was determined to be 0.92, relative to that of naphthalene. Efforts to gain a better understanding of the luminescent mechanism of **1** are being undertaken by our group.

As we anticipated, compound **1** is remarkably stable towards air in the solid state. In fact, it can be kept under air for days without decomposition. Compound **1** is also thermally stable. It melts at 290 °C without decomposition and can be sublimed at *ca.* 150 °C and 0.06 mmHg. The high stability of compound **1** can be attributed to both the presence of the bridging O atom and the covalency of B–C and B–N bonds, in comparison to the corresponding aluminium compounds. To our best knowledge, compound **1** is the first example of blue luminescent boron compounds. The high stability and volatility of **1** make it a good candidate as an emitter in electroluminescence display devices, which is being investigated in our laboratory.

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Footnotes and References

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† *Crystal data for 1*: $a = 12.865(4)$, $b = 10.085(3)$, $c = 13.476(4)$ Å, $\beta = 103.81(2)^\circ$, $U = 1698.0(8)$ Å³, monoclinic, space group $P2_1/n$. Data were collected over the range 2θ 3–45° at 25 °C on a Siemens P4 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å), operated at 50 kV and 40 mA. Data were processed on a Pentium PC using Siemens SHELXTL software package. Convergence to the final R values of $R_1 = 0.0678$, $wR_2 = 0.1840$ for **1** were achieved by using 2193 reflections [$I > 2\sigma(I)$] and 218 parameters. Details of X-ray crystallographic analyses are given in supplementary material available from the authors. CCDC 182/707. Elemental analysis for C₁₈H₂₀B₂N₄O: calc. C, 65.51; H, 6.07; N, 16.98. Found: C, 65.35; H, 6.03; N, 16.80%. ¹H NMR (CDCl₃): δ 0.95 (t, 6 H, CH₃), 1.26 (q, 4 H, CH₂), 6.41 (d, 2 H, 7-azain), 7.04 (m, 2 H, 7-azain), 7.45 (d, 2 H, 7-azain), 7.97 (m, 2 H, 7-azain), 8.12 (m, 2 H, 7-azain). Excitation and emission spectra for compound **1** and the free ligand were recorded on a Photon Technologies International QM1 spectrometer. The solution spectra for both compounds were recorded under the same conditions except that the molar concentration of the free ligand was made 5.44 times higher than that of the boron compound owing to its low emission intensity.

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