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Syntheses and structures of new blue luminescent B(III) and Al(III) complexes: BPh_2(acac-azain) and $Al(CH_3)$(acac-azain)$_2$, acac-azain = 1-*N*-7-azaindolyl-1,3-butanedionato

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Abstract

A novel blue luminescent ligand, 1-*N*-7-azaindolyl-1,3-butanedione (acac-azainH), has been synthesized and characterized structurally. The acac-azainH has a diketone structure in the solid state. The diketone form of acac-azainH is also dominant in solution. The acac-azainH molecule reacts readily with BPh_3 and $Al(CH_3)_3$ to form chelate complexes BPh_2(acac-azain) (**1**) and $Al(CH_3)$(acac-azain)$_2$ (**2**), respectively. The structure of **1** was determined by a single-crystal X-ray diffraction analysis. The acac-azainH molecule and compounds **1** and **2** are all blue luminescent but the luminescent efficiency is poor. In solution, compound **2** appears to exist in two isomeric forms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Aluminum; Luminescence; Azaindolyl

1. Introduction

Blue luminescent compounds are an important class of molecules that have been highly sought-after recently by scientists around the world because of their potential applications in electroluminescent devices [1]. A few years ago we reported that 7-azaindole ligands are capable of binding to boron(III), aluminum(III) or zinc(II) readily to produce bright blue luminescent complexes [2]. We have demonstrated that some of these blue luminescent complexes can be used as blue emitters in electroluminescent devices. Our recent efforts focus on the modification of 7-azaindole ligand so that more stable and efficient blue emitters could be obtained. Acetylacetonato (acac) and its derivatives (acac*) are the best known chelate ligands for metal ions. Metal complexes of acac or acac* often display a high stability and a high volatility, in comparison to other chelate complexes [3]. Consequently, many metal acac and acac* complexes have been frequently used as precursor molecules for a number of metal and metal oxide materials. Recently, diketone boron complexes have been found to be useful electroluminescent materials [4]. Therefore, we investigated the synthesis of an acac 7-azaindole derivative (1-*N*-7-azaindolyl-1,3-butanedione, acac-azainH) and its boron and aluminum complexes. The results are reported herein.

2. Experimental

All the starting materials were purchased from Aldrich Chemical Co. All the syntheses were carried out under a nitrogen atmosphere. Solvents were freshly distilled over appropriate drying reagents prior to use. ^{1}H-NMR spectra were recorded on Bruker Advance 300 or 400 MHz spectrometers. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model 2 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Ltd, Delta, British Columbia. Melting points were determined on a Fisher–Johns melting point apparatus.

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2.1. Synthesis of 1-N-7-azaindolyl-1,3-butanedione (acac-azainH)

A solution of diketene (0.420 g, 5 mmol) in 5 ml of toluene was added dropwise into a solution of 7-azaindole (0.590 g, 5 mmol) in 10 ml of toluene over a period of 10 min. The reaction mixture was then heated to 90 °C for 2 h. After the solvent was removed, the residue was purified by column chromatography using 1:2 ethyl acetate–hexanes as eluent, yielding colorless solid of acac-azainH (0.935 g, yield 92.5%), m.p. 77–79 °C. ^{1}H-NMR ($CDCl_3$, 25 °C): the enol isomer, $\delta =$ 13.90 (s, 1H, OH), 8.41 (d, $^3J = 4.8$ Hz, 1H; azain), 8.07 (d zH, $^3J = 4.2$ Hz, 1H; azain), 7.92 (m zH, 1H; azain), 7.56 (s, 1H; C=C–H), 7.21 (m, 1H; azain), 6.65 (m, 1H; azain), 2.23 (s, 3H; CH_3); the diketone isomer: 8.32 (d zH, $^3J = 4.5$ Hz, 1H; azain), 8.02 (d zH, $^3J = 3.9$ Hz, 1H; azain), 7.92 (m zH, 1H; azain), 7.21 (m, 1H; azain), 6.65 (m, 1H; azain), 4.65 (s, 2H; CH_2), 2.43 (s, 3H; CH_3). Anal. Calc. for $C_{11}H_{10}N_2O_2$: C, 65.35; H, 4.95; N, 13.86. Found: C, 65.42; H, 4.98; N, 13.92%.

2.2. Synthesis of BPh$_2$(acac-azain) (**1**)

Triphenylboron (0.121 g, 0.5 mmol) was added to a solution of acac-azainH (0.100 g, 0.5 mmol) in 15 ml of THF. The mixture was stirred and refluxed for 4 h. After the mixture was cooled to ambient temperature, the solvent was removed under vacuum. Recrystallization from CH_2Cl_2–hexanes yielded colorless crystals of **1** (0.153 g, yield 83%), m.p. 180–182 °C. ^{1}H-NMR ($CDCl_3$, 25 °C): $\delta = 8.41$ (dd, $^3J_1 = 4.8$ Hz, $^3J_2 = 1.5$ Hz, 1H, azain), 8.15 (d, $^3J = 5.1$ Hz,1H, azain), 7.94 (dd, $^3J_1 = 7.8$ Hz, $^3J_2 = 1.8$ Hz, 1H, azain), 7.77 (s, 1H; C=C–H), 7.57, 7.25 (m, 11H, phenyl, azain), 6.76 (d zH, $^3J = 4.2$ Hz, 1H, azain), 2.45 (s, 3H; CH_3). Anal. Calc. for $C_{23}H_{19}O_2N_2B$: C, 75.41; H, 5.19; N, 7.65. Found: C, 75.23; H, 5.27; N 7.59%.

Table 1
Crystal data and structure refinement parameters

Compound	Acac-azainH	**1**
Empirical formula	$C_{11}H_{10}N_2O_2$	$C_{23}H_{19}BN_2O_2$
Formula weight	202.21	366.21
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.6053(14)	9.978(3)
b (Å)	13.267(3)	13.283(5)
c (Å)	10.049(2)	14.457(4)
α (°)	90	90
β (°)	93.331(4)	96.85(2)
γ (°)	90	90
V (Å^3)	1012.2(3)	1902.6(10)
Z	4	4
D_{calc} (g cm^{-3})	1.327	1.279
T (K)	294	296
μ (cm^{-1})	0.94	0.81
2θ, max (°)	56.58	50
Reflections measured	7271	3547
Reflections used	2416	3343
Parameters	176	253
Final R [$I > 2\sigma(I)$]	R_1 [a] $= 0.0378$	$R_1 = 0.0513$
	wR_2 [b] $= 0.1067$	$wR_2 = 0.1164$
R (all data)	$R_1 = 0.0587$	$R_1 = 0.0904$
	$wR_2 = 0.1157$	$wR_2 = 0.1370$
Goodness-of-fit on F^2	1.040	1.018

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

2.3. Synthesis of Al(CH$_3$)(acac-azain)$_2$ (**2**)

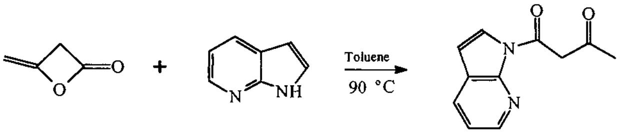
After a solution of acac-azainH (1.212 g, 6 mmol) in 35 ml of toluene was cooled down to − 78 °C in an acetone–liquid nitrogen bath, 1 ml of $Al(CH_3)_3$ (2 mmol, 2 M solution in toluene) was added dropwise. The mixture was stirred at − 78 °C for 2 h, and then warmed to ambient temperature and stirred overnight. The solution was concentrated by vacuum. White precipitate was recrystallized from toluene–hexanes to afford white crystals of **2** (0.795 g, yield 89%). ^{1}H-NMR ($CDCl_3$, 25 °C): $\delta = 8.440$ (m, 2H, azain), 8.06 (m, 2H, azain), 7.88 (m, 2H, azain), 7.63, 7.62, 7.61 (s zH, 2H, C=C–H), 7.19 (m, 2H, azain), 6.50 (m, 2H, azain), 2.31, 2.29, 2.28 (s, 6H, C–CH_3), 0.089 (s, 3H, Al–CH_3). Anal. Calc. for $C_{23}H_{21}O_4N_4Al$: C, 62.16; H, 4.73; N, 12.61. Found: C, 61.58; H, 4.26; N, 12.42%.

2.4. X-ray crystallography analysis

All crystals were mounted on glass fibers. The data for acac-azainH and **1** were collected on a Bruker SMART CCD 1000 X-ray diffractometer and a Siemens P4 X-ray diffractometer, respectively, with graphite-monochromated Mo–K$_\alpha$ radiation, operating at 50 kV and 30 mA at 293 K. The data collection range over 2θ is 5.10–56.58° for acac-azainH and 4.12–50.00° for **1**, respectively. No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10) [5]. Neutral atom scattering factors were taken from Cromer and Waber [6]. Empirical absorption corrections were applied for both crystals. Crystals of both acac-azainH and **1** belong to the monoclinic space group $P2_1/c$. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms for acac-azainH were located directly from the difference Fourier maps. The hydrogen atoms in **1** were either determined directly from the difference Fourier maps or calculated. The crystal data are summarized in Table 1. Selected bond lengths and angles for acac-azainH and **1** are given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°)

Acac-azainH			
Bond lengths		*Bond angles*	
O(1)–C(8)	1.2118(15)	C(1)–N(1)–C(8)	122.11(12)
O(2)–C(10)	1.2127(14)	C(1)–N(1)–C(7)	106.67(12)
C(8)–C(9)	1.4876(19)	C(8)–N(1)–C(7)	131.22(10)
C(9)–C(10)	1.5129(17)	O(1)–C(8)–N(1)	118.79(13)
C(10)–C(11)	1.483(2)	O(1)–C(8)–C(9)	122.72(13)
N(1)–C(8)	1.4068(17)	N(1)–C(8)–C(9)	118.48(11)
		O(2)–C(10)–C(11)	122.83(13)
		O(2)–C(10)–C(9)	120.65(11)
		C(11)–C(10)–C(9)	116.51(12)
		O(2)–C(10)–C(11)	122.83(13)
1			
Bond lengths		*Bond angles*	
O(2)–B(1)	1.546(3)	C(16)–N(1)–C(17)	123.68(19)
C(7)–B(1)	1.596(3)	C(16)–N(1)–C(23)	128.83(19)
C(1)–B(1)	1.605(3)	C(17)–N(1)–C(23)	107.42(19)
O(1)–B(1)	1.528(3)	O(2)–C(16)–N(1)	113.7(2)
O(2)–C(16)	1.288(3)	O(2)–C(16)–C(15)	122.6(2)
O(1)–C(14)	1.294(3)	N(1)–C(16)–C(15)	123.7(2)
N(1)–C(16)	1.382(3)	O(1)–C(14)–C(15)	122.4(2)
C(16)–C(15)	1.384(3)	O(1)–C(14)–C(13)	115.3(2)
C(14)–C(15)	1.374(3)	C(15)–C(14)–C(13)	122.3(2)
C(14)–C(13)	1.488(3)	O(1)–B(1)–O(2)	106.60(17)
		O(1)–B(1)–C(7)	108.27(19)
		O(2)–B(1)–C(7)	107.43(19)
		O(1)–B(1)–C(1)	109.19(19)
		O(2)–B(1)–C(1)	108.70(19)
		C(7)–B(1)–C(1)	116.23(19)
		C(2)–C(1)–C(6)	115.7(2)
		C(2)–C(1)–B(1)	120.2(2)
		C(6)–C(1)–B(1)	124.2(2)
		C(12)–C(7)–C(8)	116.1(2)
		C(12)–C(7)–B(1)	121.2(2)
		C(8)–C(7)–B(1)	122.6(2)



Scheme 1.

3. Results and discussion

3.1. Syntheses and structures

3.1.1. The acac-azainH molecule

The synthesis of the acac-azainH ligand was carried out using a modified literature method reported previously for related compounds[7] in high yield (Scheme 1). The structure of acac-azainH was determined by a single-crystal X-ray diffraction analysis. It is well known that 1,3-diketone molecules have two isomeric forms—the enol form and the diketone form. As shown in Fig. 1, the acac-azainH molecule adopts the diketone form in the solid state. The C(8)–O(1) and C(10)–O(2) distances of 1.2118(5) and 1.2127(14) Å are typical of C–O double bond lengths, supporting the diketone structure. The two carbonyl groups of the diketone are oriented away from each other. One of the carbonyl groups, adjacent to the indole ring, is coplanar with the 7-azaindolyl portion. The N(1)–C(8) bond length of 1.4068(17) Å is much shorter than a single bond length, indicative of the conjugation of the carbonyl group with the indole ring. The C(9) atom has a typical tetrahedral geometry, and the C(8)–C(9) and C(9)–C(10) bond lengths are typical of single bonds, consistent with the diketone structure. The behavior of acac-azainH in solution was examined by ^{1}H-NMR spectroscopy, which revealed that in solution the diketone form and the enol form are in equilibrium with the diketone form being the dominant species (~ 3:1 ratio). The diketone form of the acac-azainH molecule is clearly stabilized by the conjugation of the C(8) carbonyl group with the indole ring, as shown by the crystal structure. The acac-azainH molecule is not stable in alcohol solution, especially in the presence of base, which catalyzes the substitution of the 7-azaindolyl group in acac-azainH by an alkoxy group to form the corresponding ester. Similar substitution reactions for 1,3-diketone molecules have been well documented [8].

3.1.2. The complexes of acac-azain

Two novel coordination compounds of acac-azain have been obtained, namely BPh$_2$(acac-azain) (**1**) and Al(CH$_3$)(acac-azain)$_2$ (**2**). Compound **1** was obtained by the reaction of acac-azainH with BPh$_3$ in a 1:1 ratio while compound **2** was obtained from the reaction of acac-azainH with Al(CH$_3$)$_3$ in a 3:1 ratio, intended for the synthesis of Al(acac-azain)$_3$. Our attempts to synthesize Al(acac-azain)$_3$ by using excess acac-azainH were unsuccessful, which, we believe, is likely due to the steric hindrance imposed by the coordinated acac-azain

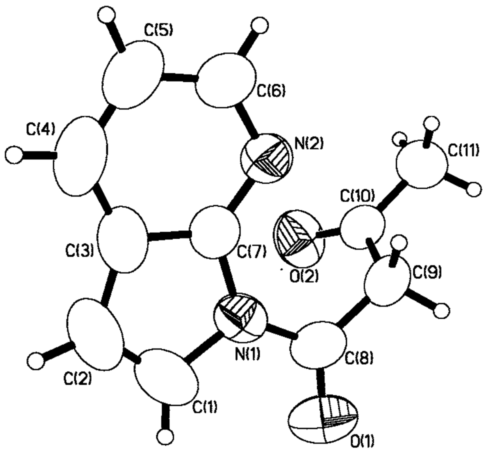


Fig. 1. A diagram showing the structure of acac-azainH with 50% thermal ellipsoids and labeling schemes.

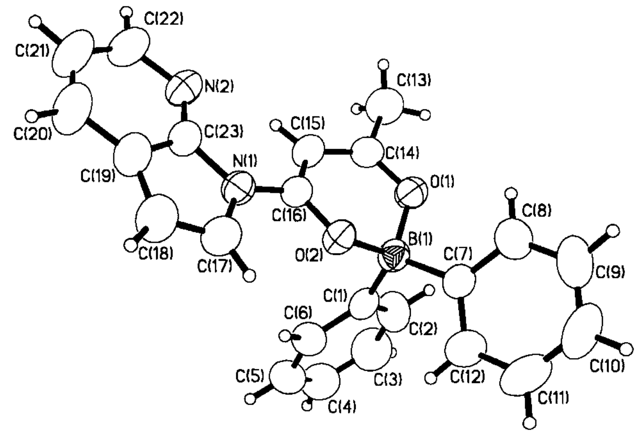


Fig. 2. A diagram showing the structure of **2** with 50% thermal ellipsoids and labeling schemes.

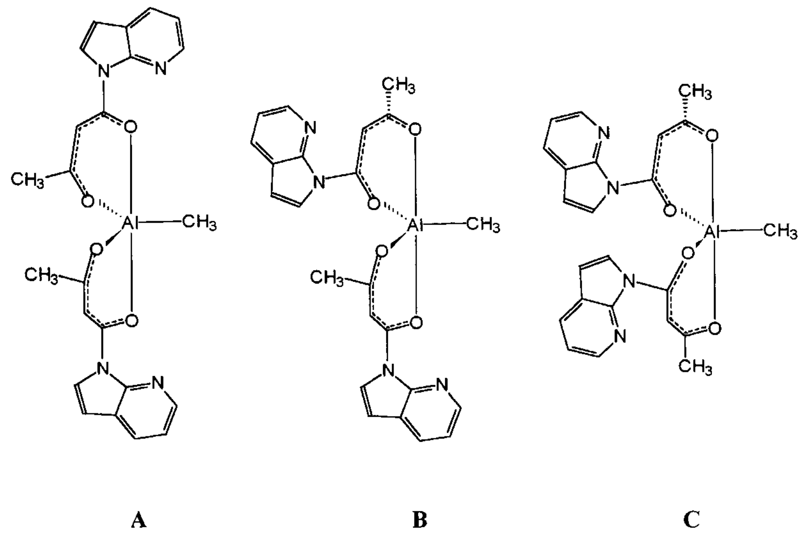
ligands that prevent the replacement of the third methyl group. Compound **1** was fully characterized by ^{1}H-NMR spectroscopy, elemental and single-crystal X-ray diffraction analyses. Attempts to obtain single-crystals of **2** were unsuccessful.

The structure of **1** is shown in Fig. 2. The boron center of **1** has a tetrahedral geometry, similar to those displayed by BPh_2(mqp) and BR_2(q) compounds [9,10] (mqp = 2-(4′-methylquinolinyl)-2-phenolato, q = 8-hydroxylquinolinato). The B–C and B–O bond lengths are comparable to those of previously known boron compounds [11–13]. Several crystal structures of diketone boron compounds have been reported previously [15]. The acac-azain ligand chelates to the boron center through both oxygen atoms in a typical acac fashion, forming a six-membered chelate ring with the boron center. The C(16)–N(1) bond that connects the 7-azaindolyl portion with the diketone portion, is shorter than that of the free neutral ligand. The C(14)–C(15) and C(15)–C(16) bond lengths (1.374(3) and 1.384(3) Å) of the acac-azain ligand are much shorter than the corresponding ones in the free neutral ligand and are typical of chelated acac and acac* ligands.

Compound **2** was characterized by ^{1}H-NMR spectroscopy and elemental analysis. In solution, compound **2** appears to exist in several isomeric forms, as evidenced by the observation of three C–CH_3 chemical shifts (in ~ 1:1:2 ratio) and three –C=C–H chemical shifts (in ~ 1:2:1 ratio) in the ^{1}H-NMR spectrum of **2** (Only one Al–CH_3 chemical shift is observed, which may be due to accidental overlap or the insensitivity of the Al–CH_3 group to the location of the 7-azaindolyl group.). We believe that compound **2** is most likely a five-coordinate mononuclear species. The most common coordination geometry for five-coordinate Al(III) complexes with monodentate or bidentate ligands is trigonal bipyramidal (tbp) [2a,14]. Assuming that compound **2** adopts the tbp geometry, three geometric isomers are possible, as shown in Scheme 2. The most plausible explanation of the ^{1}H-NMR spectrum of **2** is that isomers **A** and **B** (Isomer **C** is the least likely because of the steric interactions between the two 7-azaindolyl groups.) coexist in solution. This could also explain the fact that we have not been able to grow single-crystals of **2**.

3.1.3. Luminescence

7-Azaindole emits at 360 nm in solution (toluene or CH_2Cl_2) and the solid state. In contrast, the acac-azainH molecule has a broad emission band at $\lambda = 420$ nm in the solid state (excitation at 360 nm), and at $\lambda = 429$ nm in solution (CH_2Cl_2, excitation at 306 nm), as shown in Fig. 3. The excitation band in solution has ~ 50 nm blue-shift with respect to that of the solid. Although the acac-azainH is blue luminescent, it has a



Scheme 2.

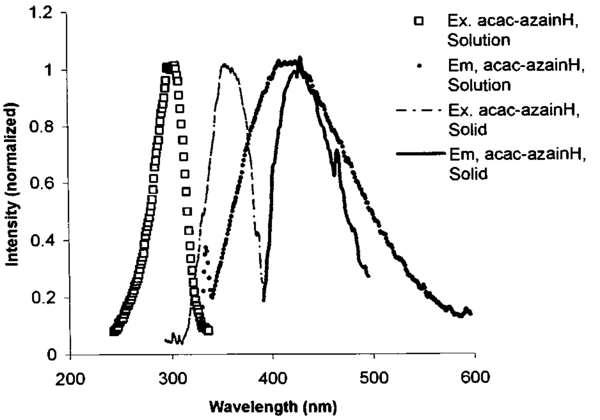


Fig. 3. Excitation and emission spectra of acac-azainH.

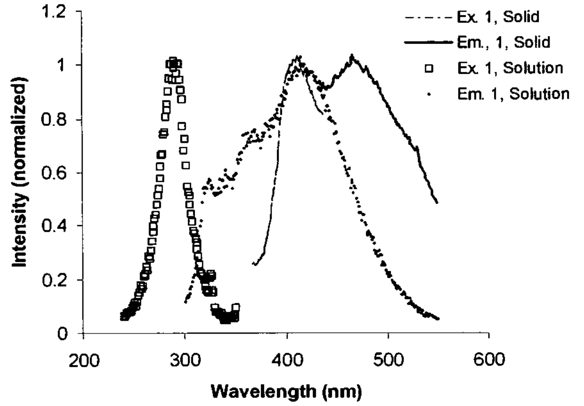


Fig. 4. Excitation and emission spectra of 1.

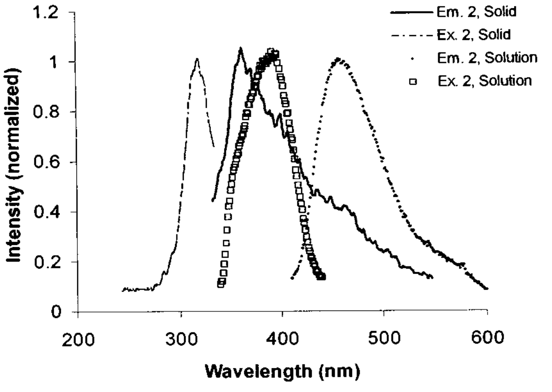


Fig. 5. Excitation and emission spectra of 2.

very low emission efficiency (quantum yield = 0.68%, relative to that of 9,10-diphenylanthracene). The boron complex **1** has very weak blue luminescence in solution and the solid state. The emission band maximum of **1** is at $\lambda = 419$ nm in solution (CH_2Cl_2, excitation at 295 nm) and $\lambda = 470$ nm in the solid state (excitation at 415 nm) (Fig. 4). The quantum yield of **1** was determined to be 0.07%, relative to that of 9,10-diphenylanthracene. The luminescence of the aluminum complex **2** appears to be visibly brighter than compound **1**, with the emission maximum at $\lambda = 460$ nm in solution (CH_2Cl_2, excitation at 397 nm). Due to the poor stability of **2**, a reliable quantum yield for **2** could not be obtained. In the solid state, compound **2** has a broad emission band, covering 320–560 nm, with the maximum at $\lambda = 364$ nm (excitation at 320 nm) (Fig. 5). Many factors such as inter-molecular interactions (No parallel π–π stacking was observed in the crystal lattice of **1**.) and the formation of exciplexes could contribute to the observed spectral difference from solution to the solid state for compounds **1** and **2**. The detail is however yet to be understood.

Previously we have demonstrated that the attachment of 7-azaindolyl to organic units other than carbonyl groups, such as phenyl, biphenylyl, or pyridyl, resulted in the formation of very bright blue luminescent organic molecules [2f,15]. The unexpected poor emission efficiency of the acac-azainH molecule and compound **1** is therefore likely caused by the carbonyl groups of the diketone portion, that perhaps quenches the luminescence of the attached 7-azaindolyl group. The poor emission efficiency of **1** and the poor stability of **2** make them unsuitable as emitters for electroluminescent devices. Therefore, we did not carry out the study of their performance in electroluminescent devices.

In summary, we have demonstrated that the novel acac-azain ligand is capable of chelating to Al(III) and B(III) centers but the resulting complexes display blue luminescence that is too weak for practical applications.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 164267 and 164268 for acac-azainH and compound **1**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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