Organometallics **2000,** *19,* 5709−5714

Syntheses, Structures, and Luminescence/Electroluminescence of BPh_2(mqp), $Al(CH_3)(mqp)_2$, and $Al(mqp)_3$ (mqp = 2-(4′-Methylquinolinyl)-2-phenolato)

Shi-Feng Liu,† Corey Seward,† Hany Aziz,‡ Nan-Xing Hu,‡ Zoran Popović,‡ and Suning Wang*,†

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada, and Xerox Research Center of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada

Received August 9, 2000

Three new complexes BPh_2(mqp) (**1**), $Al(CH_3)(mqp)_2$ (**2**), and $Al(mqp)_3$ (**3**) have been synthesized and characterized, where mqp = 2-(4′-methylquinolinyl)-2-phenolato. The mqp ligand in compounds **1** and **2** act as a chelate ligand, while in compound **3** it acts as both a chelate ligand and a terminal ligand. The boron center in **1** has tetrahedral geometry, while the aluminum ion in **2** and **3** has trigonal-bipyramidal geometry. In CH_2Cl_2 solution, these compounds emit a green, a green-blue, and a whitish blue color (λ = 514, 515, 497 nm), respectively, when irradiated by UV light. In the solid state, these three compounds emit a green, a blue, and a whitish blue color, respectively (λ = 520, 474, 500 nm). Electroluminescent devices using compound **3** as an emitter have been fabricated.

Introduction

The best known electroluminescent (EL) metal chelate compound is $Al(q)_3$, where q is the 8-hydroxyquinolinato ligand.[1] $Al(q)_3$ is not only a good green emitter but also a highly efficient electron-transporting material in EL devices.[2,3] To improve the performance of $Al(q)_3$, various modifications of the 8-hydroxyquinoline ligand have been investigated. It has been demonstrated that one could shift the emission color of the complex by modifying the 8-hydroxyquinoline ligand or the coordination environment around the aluminum ion in the complex.[4] In addition to the modification of the 8-hydroxyquinoline ligand, extensive research on the development of new chelate compounds containing nitrogen and oxygen donor atoms has also been carried out, the most notable of which are chelate compounds based on benzoxazole, oxadiazole, and their derivatives.[5] In search of new chelate compounds that have potential applications in electroluminescent devices, we investigated aluminum and boron chelate compounds containing the 2-(4′-methylquinolinyl)-2-phenolato (mqp) ligand. The quinolinyl portion of the mqp ligand is related to 8-hydroxyquinoline, thus ensuring the occurrence of luminescence. The attachment of a phenol group at the 2-position would allow the ligand to form chelate compounds with metal ions similarly to 8-hydroxyquinoline. Indeed, we have found that the mqp ligand readily forms a variety of luminescent complexes with aluminum(III) and boron(III) ions. The syntheses, structures, and luminescent and electroluminescent properties of three novel boron and aluminum complexes of mqp are presented herein.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. All syntheses were carried out under a nitrogen atmosphere. Solvents were freshly distilled over appropriate drying reagents prior to use. ^1H NMR spectra were recorded on Bruker Avance 300 MHz spectrometers. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model C-60 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. TLC was carried out on SiO_2 (silica gel F254, Whatman). Flash chromatography was carried out on silica (silica gel 60, 70−230 mesh). Melting points were determined on a Fisher-Johns melting point apparatus.

Synthesis of 2-(4′-Methylquinolinyl)-2-phenol (mqpH). The synthesis of mqpH involves three steps as described below.

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† Queen's University.

‡ Xerox Research Center of Canada.

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10.1021/om0006918 CCC: \$19.00

(a) (2-Methoxyphenyl)boronic Acid. *n*-Butyllithium (1.6 M in hexane, 25 mL, 40 mmol) was added to a solution of 2-bromoanisole (4.98 mL, 40 mmol) in 20 mL of THF at −78 °C under nitrogen. The mixture was stirred for 1 h and transferred to a solution of $B(OMe)_3$ (9.1 mL, 80 mmol) in 10 mL of THF at −78 °C under nitrogen, and this mixture was warmed to room temperature. After the mixture had been stirred overnight, HCl (10%, 20 mL) was added to it and stirring was continued for 10 min. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with brine twice and dried over anhydrous sodium sulfate. After removal of solvents, the residue was added to NaOH (3.2 g, 80 mmol) in 60 mL of ethanol and the mixture was stirred for 20 min at room temperature. Water (50 mL) was added to the residue after the solvent was evaporated. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed with brine and dried over sodium sulfate. The residue was recrystallized from diethyl ether/hexane to give colorless crystals of (2-methoxyphenyl)boronic acid (3.7 g, yield 61%). Mp: 88−90 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.82 (1H, m), 7.42 (1H, m), 6.80−7.04 (2H, m), 5.87 (2H, s), 3.93 (3H, s).

(b) 2-(4′-Methylquinolinyl)anisole. A solution of 2-chlorolepidine (1.78 g, 10 mmol) in 10 mL of anhydrous 1,2-dimethoxyethane (DME) was added under nitrogen to a solution containing a catalyst prepared by reaction of $Pd(PPh_3)_2Cl_2$ (0.28 g, 0.40 mmol) in 5 mL of anhydrous DME with diisobutylaluminum hydride (1.0 M in hexane, 0.8 mL, 0.80 mmol). After the mixture had been stirred at room temperature for 15 min, (2-methoxyphenyl)boronic acid (1.52 g, 10 mmol) and sodium ethoxide (2.0 M in ethanol, 10 mL, 20 mmol) were added successively. The resulting mixture was heated at reflux for 5 h under N_2 and cooled to room temperature. The suspension was filtered through Celite to give a clear solution. The Celite was washed with CH_2Cl_2. The solution was concentrated to give a brown residue, which was purified by column chromatography using 4/1 hexane/ethyl acetate as the eluent, yielding a white solid of 2-(4′-methylquinolinyl)anisole (2.12 g, 85%). Mp: 76−77 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.20 (1H, d, J = 8.4 Hz), 8.02 (1H, m), 7.82 (1H, dd, J = 7.6 Hz, 1.8 Hz), 7.69−7.75 (2H, m), 7.54−7.60 (1H, m), 7.41−7.47 (1H, m), 7.11−7.17 (1H, m), 7.05 (1H, d, J = 8.2 Hz), 3.87 (3H, s), 2.75 (3H, s).

(c) 2-(4′-Methylquinolinyl)-2-phenol (mqpH). A solution of 2-(4′-methylquinolinyl)anisole (1.52 g, 6.1 mmol) in 25 mL of dichloromethane was added to a solution of BBr_3 (1.0 M in hexane, 6.1 mL, 6.1 mmol) at −78 °C under nitrogen. The reaction mixture was warmed to room temperature and stirred overnight. H_2O (40 mL) was then added, and the resulting mixture was stirred for 20 min. The organic phase was separated. The aqueous layer was neutralized with saturated Na_2CO_3 to pH 6 and was extracted with $CHCl_3$ (3 × 40 mL). The combined organic phases were washed with brine and dried over sodium sulfate. After the solvent was removed, the residue was purified by column chromatography using 4/1 hexane/ethyl acetate as the eluent, yielding a yellow-orange solid of 2-(4′-methylquinolinyl)phenol (0.89 g, yield 63%). Mp: 79−81 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.06 (1H, d, J = 8.4 Hz), 8.02 (1H, d, J = 8.5 Hz), 7.98 (1H, dd, J = 8.1 Hz, 1.3 Hz), 7.91 (1H, s), 7.73−7.78 (1H, m), 7.57−7.62 (1H, m), 7.32−7.41 (1H, m), 7.11 (1H, d, J = 8.2 Hz), 6.95−7.00 (1H, m), 2.83 (3H, s). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.17; H, 5.52; N, 5.88.

Synthesis of BPh_2(mqp) (1). Triphenylborane (242 mg, 1.00 mmol) was added to 20 mL of a THF solution containing 0.235 g (1 mmol) of mqpH under N_2. The mixture was stirred and heated at reflux for 4 h. After the mixture was cooled to ambient temperature, it was concentrated under vacuum and transferred to a drybox. The residue was recrystallized from CH_2Cl_2/hexane to give a yellow crystalline product (296 mg, yield 74%). Mp: 210 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, 298 K): 8.20 (1H, d, J = 9.0 Hz), 8.03 (1H, dd, J = 8.2, 1.3 Hz), 7.97 (1H, s), 7.70 (1H, dd, J = 8.0, 1.2 Hz), 7.50 (1H, m), 7.25−7.40 (7H, m), 7.12−7.24 (5H, m), 7.09 (1H, d, J = 8.2 Hz), 6.87 (1H, m), 2.82 (3H, s). Anal. Calcd for $C_{28}H_{22}NOB$: C, 84.22; H, 5.55; N, 3.50. Found: C, 83.17; H, 5.87; N, 3.39. (This sample was analyzed twice using crystals, but the carbon content is consistently low.)

Synthesis of $Al(CH_3)(mqp)_2$ (2). Trimethylaluminum (2.0 M in toluene, 0.10 mL, 0.20 mmol) was added slowly to 15 mL of a toluene solution containing mqpH (141 mg, 0.60 mmol) at ambient temperature under N_2. The mixture was stirred for 3 h at ambient temperature, concentrated, and recrystallized from CH_2Cl_2/toluene. Colorless crystals of **2** (74 mg, yield 73%) were obtained. Mp: 130 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, 298 K): 8.55 (2H, m), 8.03 (2H, dd, J = 8.1, 1.3 Hz), 7.86 (2H, s), 7.81 (2H, d, J = 7.5 Hz), 7.57−7.70 (4H, m), 7.18−7.36 (4H, m), 6.96 (2H, m), 2.83 (6H, s), −0.34 (3H, s). Anal. Calcd for $C_{33}H_{27}N_2O_2Al$: C, 77.63; H, 5.33; N, 5.49. Found: C, 77.83; H, 5.47; N, 5.06.

Synthesis of $Al(mqp)_3$ (3). Trimethylaluminum (2.0 M in toluene, 0.10 mL, 0.20 mmol) was added slowly to 15 mL of a THF solution containing mqpH (164 mg, 0.70 mmol) at ambient temperature under N_2. The mixture was stirred for 3 h at ambient temperature, concentrated, and recrystallized from CH_2Cl_2/hexane. Light yellow crystals of **3** (93 mg, yield 64%) were obtained. Mp: 213−215 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, 298 K): 8.33 (3H, d, J = 8.4 Hz), 7.90 (3H, d, J = 7.5 Hz), 7.75 (3H, s), 7.71 (3H, d, J = 7.4 Hz), 7.48 (3H, m), 7.39 (3H, m), 7.05 (3H, m), 6.80 (3H, t, J = 7.4 Hz), 6.31 (3H, d, J = 8.2 Hz), 2.81 (3H s), 2.55 (6H, s). Anal. Calcd for $C_{48}H_{36}N_3O_3Al\cdot 0.5CH_2Cl_2$: C, 75.43; H, 4.83; N, 5.44. Found: C, 75.30; H, 4.87; N, 5.42.

Fabrication of Electroluminescent Devices. The EL devices using **3** as the emitting layer were fabricated on an indium−tin oxide (ITO) substrate. Organic layers and a metal cathode composed of magnesium silver alloy ($Mg_{0.9}Ag_{0.1}$) were deposited on the substrate by conventional vapor vacuum deposition. Prior to the deposition, *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) and Al(q)$_3$ were purified via a train sublimation method.[6] Train sublimation of **3** was unsuccessful. Therefore, crystals of compound **3** obtained from repeated recrystallization were used for film deposition. NPB was used as the hole transport material in all devices, and Al(q)$_3$ was used as the electron transport material in one of the devices. The device structures and the thickness of each layer are listed in Table 3. To obtain the photoluminescence (PL) spectra, a thin film (100 nm) deposited on a quartz substrate was measured with a fluorescence spectrophotometer. The current/voltage characteristics were measured using a Keithley 238 current/voltage unit. The light intensity of the EL device was measured by a Minolta Chroma Meter, Model CS100. The EL spectrum was obtained by an in-house setup made up of a series of electronic components including a monochromator (Instruments SA Inc.), a photomultiplier tube, and a photon counter.

X-ray Crystallography Analysis. All crystals were mounted on glass fibers. The data for mqpH, **1**, and **2** were collected on a Siemens single-crystal P4 X-ray diffractometer, while the data for **3** were collected on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation operating at 50 kV and 35 mA at 23 °C. The data collection ranges over the 2θ range are 2−45° for mqpH, 4.32−47.4° for **1**, 3.50−50.0° for **2**, and 3.40−46.5° for **3**. No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS Window NT SHELXTL software package (version 5.10).[7]

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[6] Wagner, H. J.; Loutfy, R. O.; Hsiao, C. K. *J. Mater. Sci.* **1982**, *17*, 2781.

[7] SHELXTL NT Crystal Structure Analysis Package, Version 5.10; Bruker Axs, Analytical X-ray System, Madison, WI, 1999.

Table 1. Crystallographic Data

	mqpH	**1**	**2**	**3**
formula	$C_{16}H_{13}NO$	$C_{28}H_{22}NOB$	$C_{33}H_{27}N_2O_2Al{\cdot}0.5C_7H_8$	$C_{48}H_{36}N_3O_3Al{\cdot}0.5CH_2Cl_2$
fw	235.27	399.28	556.62	772.24
space group	$I2/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	22.686(7)	12.3227(14)	10.786(5)	12.4161(6)
b/Å	9.309(5)	9.684(4)	11.660(2)	14.5747(7)
c/Å	23.114(5)	17.684(9)	11.977(2)	21.2238(9)
α/deg	90	90	92.652(18)	90
β/deg	98.123(16)	95.503(14)	104.04(2)	93.0580(10)
γ/deg	90	90	92.88(3)	90
V/Å^3	4832(3)	2100.6(13)	1456.9(7)	3835.2(3)
Z	16	4	2	4
D_c/g cm^{-3}	1.294	1.263	1.269	1.337
μ/cm^{-1}	0.81	0.75	1.06	1.71
$2\theta_{max}$/deg	45	47	50	47
no. of rflns measd	3242	3265	5329	15 688
no. of rflns used (R_{int})	3145 (0.0539)	3104 (0.0293)	5040 (0.0399)	5508 (0.0175)
no. of variables	328	280	375	518
final R ($I > 2\sigma(I)$)				
R1[a]	0.0925	0.0666	0.0784	0.0522
wR2[b]	0.1550	0.1332	0.2088	0.1562
R (all data)				
R1	0.3071	0.1478	0.1458	0.0689
wR2	0.2296	0.1672	0.2749	0.1650
goodness of fit on F^2	0.986	1.029	1.051	1.053

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

Table 2. Bond Lengths (Å) and Angles (deg) for Compounds 1−3

Compound **1**			
O(1)−B(1)	1.337(5)	C(1)−B(1)	1.352(5)
N(1)−B(1)	1.483(5)	B(1)−C(7)	1.397(5)
O(1)−B(1)−C(1)	1.660(5)	C(7)−B(1)−N(1)	116.8(3)
O(1)−B(1)−C(7)	1.609(6)		105.9(3)
C(1)−B(1)−C(7)	1.617(6)		108.5(3)
O(1)−B(1)−N(1)	109.8(3)		112.3(3)
C(1)−B(1)−N(1)	102.9(3)		
Compound **2**			
Al(1)−O(2)	1.748(4)	Al(1)−N(1)	2.182(4)
Al(1)−O(1)	1.758(4)	Al(1)−N(2)	2.197(4)
Al(1)−C(33)	1.964(6)		
O(2)−Al(1)−O(1)	106.93(19)	C(33)−Al(1)−N(1)	93.1(2)
O(2)−Al(1)−C(33)	124.7(2)	O(2)−Al(1)−N(2)	87.52(16)
O(1)−Al(1)−C(33)	128.3(2)	O(1)−Al(1)−N(2)	88.50(16)
O(2)−Al(1)−N(1)	89.89(16)	C(33)−Al(1)−N(2)	91.5(2)
O(1)−Al(1)−N(1)	88.58(16)	N(1)−Al(1)−N(2)	175.36(17)
Compound **3**			
Al(1)−O(3)	1.741(2)	Al(1)−N(1)	2.120(2)
Al(1)−O(1)	1.742(2)	Al(1)−N(2)	2.133(2)
Al(1)−O(2)	1.744(2)		
O(3)−Al(1)−O(1)	125.66(10)	O(2)−Al(1)−N(1)	89.30(10)
O(3)−Al(1)−O(2)	121.02(10)	O(3)−Al(1)−N(2)	90.00(9)
O(1)−Al(1)−O(2)	113.26(11)	O(1)−Al(1)−N(2)	87.61(9)
O(3)−Al(1)−N(1)	93.22(9)	O(2)−Al(1)−N(2)	89.89(9)
O(1)−Al(1)−N(1)	89.71(10)	N(1)−Al(1)−N(2)	176.63(10)

Table 3. EL Device Data

device	hole transport[a]	emitting layer[a]	electron transport[a]	CIE (x, y)	eff,[a] cd/A
A	NPB (60)	**3** (80)		0.427, 0.475	0.21
B	NPB (60)	**3** (20)	$Al(q)_3$ (60)	0.401, 0.479	0.29

[a] The thickness (in nm) is given in parentheses. [b] Efficiency at 25 mA/cm^2.

Neutral atom scattering factors were taken from Cromer and Waber.[8] The crystals of mqpH, **1**, and **3** belong to the monoclinic space groups $I2/a$, $P2_1/c$, and $P2_1/n$, respectively, while the crystal of **2** belongs to the triclinic space group $P\bar{1}$. All structures were solved by direct methods. A disordered toluene solvent molecule was located in the lattice of **2** (0.5 toluene per molecule of **2**), while a disordered CH_2Cl_2 solvent molecule was found in the lattice of **3** (0.5 CH_2Cl_2 per molecule of **3**). There are two independent molecules in the asymmetric unit of mqpH. All non-hydrogen atoms except the disordered toluene molecule were refined anisotropically. The positions of hydrogen atoms were either determined directly from the difference Fourier maps or calculated, and their contributions in structural factor calculations were included. The crystal data are summarized in Table 1. Selected bond lengths and angles for **1**−**3** are given in Table 2.

Results and Discussion

Syntheses and Structures. The mqpH Ligand. The synthesis of 2-(4′-methylquinolinyl)-2- phenol (mqpH) is based on a modified procedure reported recently for pyridylphenols,[9] as shown in Scheme 1. The structure of mqpH was confirmed by a single-crystal X-ray diffraction analysis. As shown in Figure 1, the phenol portion of the molecule is coplanar with the quinoline portion. The hydroxy proton is shared between the oxygen and nitrogen atom. There are no intermolecular hydrogen bonds, but the unit cell packing diagram shows that there is an extended intermolecular face-to-face $\pi-\pi$ stacking between molecules of mqpH in the crystal lattice. The shortest intermolecular atomic separation distance between the stacked molecules is 3.785 Å.

Complexes of mqp. Three complexes containing the mqp ligand have been synthesized and characterized structurally. The first, $BPh_2(mqp)$ (**1**), was obtained by the reaction of BPh_3 with mqpH in a 1:1 ratio. The second, $Al(CH_3)(mqp)_2$ (**2**), was prepared by the reaction of $Al(CH_3)_3$ with mqpH in a 1:3 ratio in toluene (the excess mqpH ligand is necessary to obtain **2** in good yield). The synthesis of $Al(mqp)_3$ (**3**) could not be

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[8] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.

[9] Zhang, H.; Kwong, F. Y.; Tian, Y.; Chan, K. S. *J. Org. Chem.* **1998**, *63*, 6886−6890.

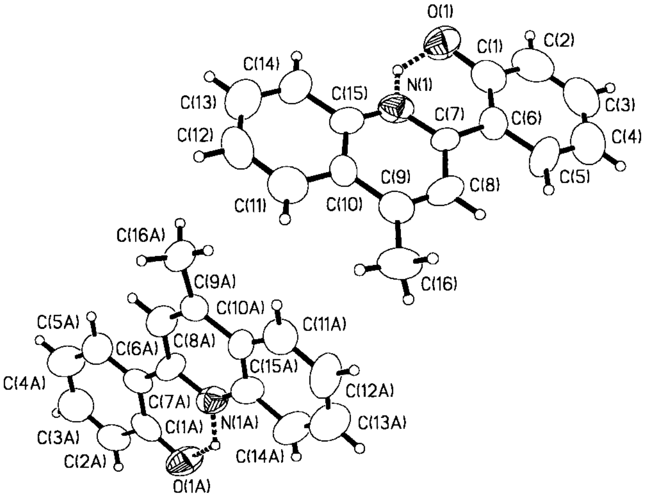
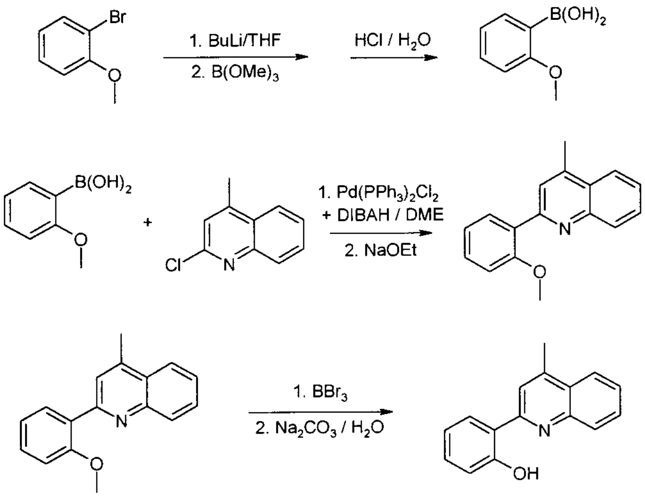


Figure 1. Diagram showing the molecular structure of mqpH with 50% thermal ellipsoids and labeling schemes.

Scheme 1



achieved in toluene even in the presence of excess mqpH. However, compound **3** could be obtained readily from the reaction of Al(CH$_3$)$_3$ with mqp in a 1:3.5 ratio in THF. THF and a slight excess of mqpH are necessary for isolating **3** and minimizing the formation of **2**. Compounds **1**−**3** have been fully characterized by ^{1}H NMR spectroscopy and elemental and single-crystal X-ray diffraction analyses. Compounds **1** and **3** are air-stable, while compound **2** decomposes slowly in the solid state when exposed to air. The melting points of **1**−**3** are 210, 130, and 213 °C, respectively, significantly higher than that of mqpH (80 °C). The high stability and high melting points of **1** and **3** make them possible candidates for electroluminescent applications.

The structure of **1** is shown in Figure 2. The boron center has typical tetrahedral geometry with B−C, B−N, and B−O bond lengths similar to those of BR$_2$(q) compounds.[3f] The mqp ligand chelates to the boron center through the oxygen and nitrogen atoms. Unlike the 8-hydroxyquinolinato ligand, which forms a planar, five-membered ring with the central atom,[1,11] the chelate ring in **1** is six-membered and puckered. A similar puckered six-membered chelate ring also was observed in 2-pyridyl-2-phenolato complexes of Co(III) and Pd(II).[12] The phenyl ring is no longer coplanar with the quinoline portion but with a dihedral angle of 19.0°.

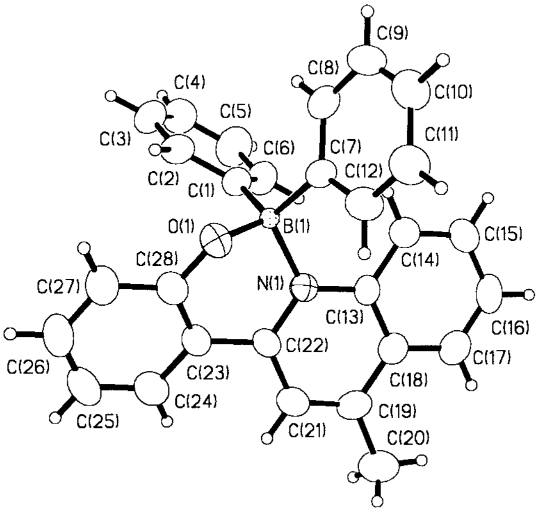


Figure 2. Diagram showing the molecular structure of **1** with 50% thermal ellipsoids and labeling schemes.

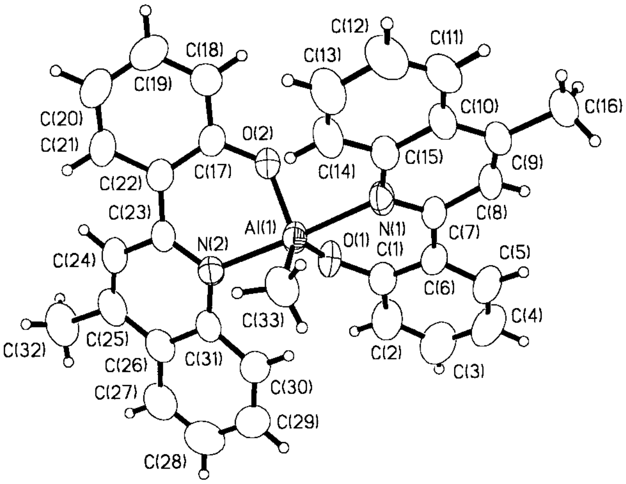


Figure 3. Diagram showing the molecular structure of **2** with 50% thermal ellipsoids and labeling schemes.

The structure of **2** is shown in Figure 3. The two mqp ligands in **2** are chelated to the Al(III) center in the same manner as observed in **1**. The Al(III) center has trigonal-bipyramidal geometry with N(1) and N(2) atoms occupying the axial positions (N(1)−Al(1)−N(2) = 175.36(17)°) and O(1), O(2), and C(33) atoms occupying the basal plane (the sum of bond angles on the basal plane is 359.9(1)°). A similar trigona-bipyramidal geometry has been observed previously in five-coordinate Al(III) complexes.[13,14] The Al−N and Al−O bond lengths in **2** are similar to those observed in Al(q)$_3$. The Al(1)−C(33) bond length (1.964(6) Å) is similar to previously reported values of five-coordinate alkylaluminum com-

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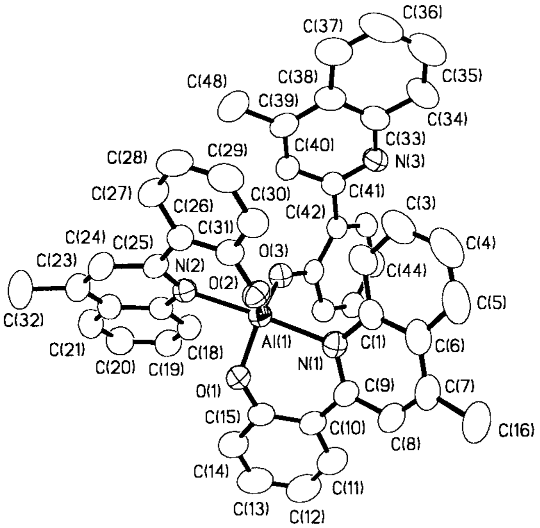

Figure 4. Diagram showing the molecular structure of **3** with 50% thermal ellipsoids and labeling schemes. For clarity, hydrogen atoms are omitted.

plexes.[13,14] As observed in **1**, the phenyl ring of the mqp ligand is not coplanar with the quinoline portion. The dihedral angles between the phenyl and the quinoline ring are 17.7 and 24.5°, respectively, for the two mqp ligands. The six-membered chelate rings are again puckered.

The structure of **3** is shown in Figure 4. In composition, compound **3** appears to be an analogue of $Al(q)_3$. Therefore, initially we anticipated that compound **3** would have a structure similar to that of $Al(q)_3$: i.e., a six-coordinate octahedron.[1] However, the crystal structure of **3** shows unequivocally that the Al(III) center in **3** is five-coordinate with a trigonal-bipyramidal geometry similar to that of **2**. The axial positions are occupied by the N(1) and N(2) atoms (N(1)−Al(1)−N(2) = 176.63(10)°), while the basal positions are occupied by the three oxygen atoms O(1), O(2), and O(3) (the sum of bond angles on the basal plane is 359.9(1)°). Two of the mqp ligands are chelated to the Al(III) center in the same manner as observed in **2**, while the third mqp ligand coordinates to the Al(III) center as a monodentate terminal ligand through the oxygen atom. The Al−N bond lengths are somewhat shorter than those of **2**, but the Al−O bond lengths are essentially the same as those of **2**. Again, the six-membered chelate rings in **3** are puckered. The dihedral angles between the phenyl ring and the quinoline ring for the two chelating mqp ligands are 27.7 and 29.7°, respectively. The increased nonplanarity of the chelating mqp ligands in **3**, compared to those in **2**, is clearly caused by the presence of the bulky terminal mqp ligand. The dihedral angle between the phenyl ring and the quinoline ring of the terminal mqp ligand is 42.4°, much larger than those of the chelating mqp ligands, attributable to steric interactions. The observed five-coordinate geometry (instead of six-coordinate) in **3** is likely caused by the increased steric interactions between mqp ligands, in comparison to the $Al(q)_3$ molecule. Compound **3** retains its five-coordinate structure in solution, as indicated by the observation of two distinct methyl resonances (due to the terminal and chelating mqp ligands) in a 1:2 integrated ratio in the ^1H NMR spectrum of **3** at ambient temperature.

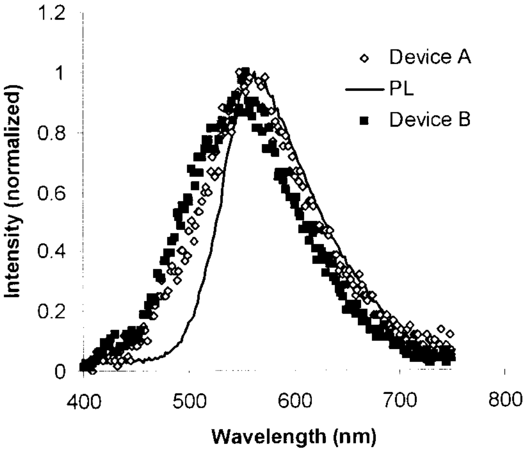

Figure 5. PL of an amorphous film of **3** and EL of devices **A** and **B**.

The structures of **1**−**3** demonstrate that the mqp ligand is capable of functioning as either a chelating ligand or a terminal ligand.

Luminescence. In the solid state, mqpH has a weak red-orange emission at λ_{max} = 579 nm. In solution (CH_3CN or CH_2Cl_2), the emission band of mqpH is shifted to λ_{max} = 482 nm. The red shift of the emission energy from solution to the solid state is mostly likely caused by the $\pi-\pi$ stacking of mqpH molecules in the solid state, as shown by the crystal structure. The emission maxima of compounds **1**−**3** in solution are at 497, 505, and 517 nm, respectively. The emission band of **3** is very broad and covers the entire 400−650 nm region. Consequently, the emission color of **3** in solution is whitish blue. The emission maxima of compounds **1**−**3** in the solid state are at 520, 474, and 500 nm, respectively, all blue-shifted in comparison to mqpH itself. The dramatic difference in emission energy displayed by mqpH and compounds **1**−**3** in the solid state can be attributed to intermolecular interactions in the solid state.

Electroluminescence. Compounds **1** and **3** are suitable candidates as emitters for electroluminescent devices because they are stable under air and have a high thermal stability (high melting points). The luminescent properties of **1** are similar to those of $BR_2(q)$ (R = ethyl, naphthyl, phenyl), investigated recently by our group.[3f] The performance of $BR_2(q)$ compounds in EL devices is not as good as that of $Al(q)_3$. Therefore, we did not conduct any investigation on the EL properties of compound **1**. Although the structure of **3** is not the same as that of $Al(q)_3$, it is a close analogue of $Al(q)_3$. Furthermore, in contrast to $Al(q)_3$, which emits a green color, compound **3** emits a whitish blue color in solution and the solid state, making it an interesting candidate for EL applications. Therefore, two EL devices using **3** as the emitter were fabricated. In both devices, NPB (*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine) is used as the hole transport layer. In device **A** no electron

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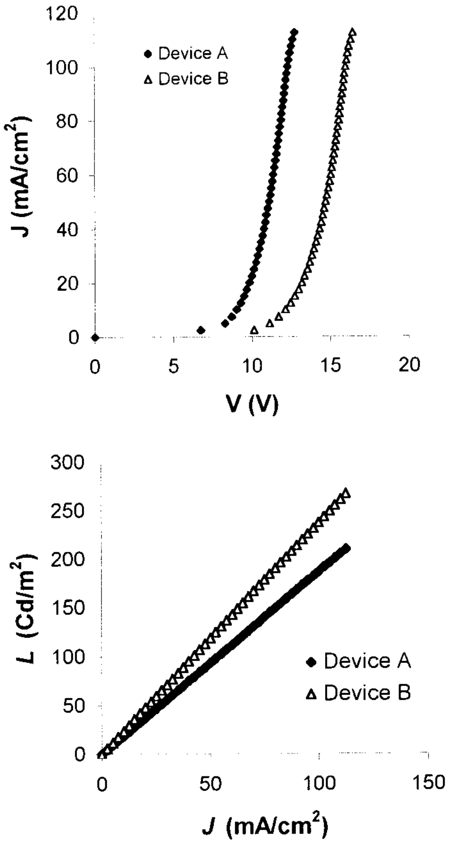

Figure 6. (top) *J*−*V* plots of devices **A** and **B**. (bottom) *L*−*J* plots of devices **A** and **B**.

transport layer is used, while in device **B** Al(q)$_3$ is used as the electron transport layer. The details of device structures and EL properties are given in Table 3.

Both devices **A** and **B** emit yellow light with an emission maximum at 560 nm. The EL spectra from devices **A** and **B** do not match the PL spectra of **3** either in solution or the solid state, but they do match the PL spectrum of an amorphous film of **3** obtained by vacuum deposition (Figure 5), indicating that the observed EL from **A** and **B** indeed originates from compound **3**. Although it is not uncommon for the PL spectrum of an amorphous film to be different from that of solution or the solid state, the difference between the PL spectra of **3** in solution, the solid state, and the film form is striking and is not understood yet. The fact that no electron transport layer is used in device **A** indicates that compound **3** can function not only as an emitter but also as an electron transport material, as Al(q)$_3$ does.

The *J*−*V* and *L*−*J* characteristics of the two devices are shown in Figure 6. The turn-on voltage for device **A** is ~8 V, while the turn-on voltage for device **B** is much higher, ~11 V. The device **B** is, however, brighter than **A**. The efficiency of device **A** is much less than that of the EL device with NPB as the hole transport layer and Al(q)$_3$ as the emitter and electron transport layer.[3f] The present experimental data indicate that compound **3** can function as an emitter and an electron transport material but its performance cannot compete with Al(q)$_3$ in EL devices. Device modification may improve the performance of **3** in EL devices, which is being investigated in our laboratory.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Xerox Research Foundation for financial support.

Supporting Information Available: Tables giving crystal data, atomic coordinates, all bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters for mqpH and **1**−**3** and a unit cell packing diagram of mqpH. This material is available free of charge via the Internet at http://pubs.acs.org.

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