# Synthesis and structures of acyclic monoanionic tetradentate aza β-diketiminate complexes of magnesium, zinc, and cadmium<sup>†</sup>

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An acyclic monoanionic tetradentate nitrogen ligand was prepared through the condensation of 2-(4-tolyl)-malondialdehyde and 8-aminoquinoline to give (BDI<sup>QQ</sup>)H where (BDI<sup>QQ</sup>)H = (8-quinolyl)-NCHC(4-tolyl)CHNH-(8-quinolyl). Metal complexes, (BDI<sup>QQ</sup>)MX, were prepared where MX = MgBr 2, ZnCl 3, and CdOAc 4. The spectroscopic and crystallographic properties of compounds 2, 3, and 4 were explored. Structures of complexes 2, 3, 4, and the tridentate ligand, (BDI<sup>Q</sup>)OH, 5, are reported.

# Introduction

Acyclic multidentate ligands containing nitrogen donors have received increased attention as analogues to Cp ligands<sup>1</sup> and for the preparation of olefin polymerization catalysts.<sup>2</sup> Several monoanionic tridentate ligands and corresponding metal complexes have been prepared.<sup>1,3-5</sup> Recently, dianionic tetradentate benzimidinate,<sup>6</sup> bisamidinate,<sup>7-9</sup> aminotroponiminates,<sup>10</sup> isoindo-line pincer<sup>11</sup> ligands and complexes have been prepared and characterized. Yet, monoanionic tetradentate nitrogen donor ligands remain relatively uncommon.

β-Diketiminate ligands represent an important class of chelating ligands that have been used across many different applications.<sup>12,13</sup> The bidentate structure of β-diketiminates has been expanded to include higher coordination numbers. Monoanionic acyclic tetradentate β-diketiminate ligands and complexes have been prepared with pendant donor groups of oxygen (Li, Ca, Mg)<sup>14-16</sup> and nitrogen (La, Sc, Yb, Pr).<sup>2,17-19</sup> A pendant arm β-diketimine iron complex, containing pyridyl donors has been synthesized but the ligand is reportedly neutral.<sup>20,21</sup>

In 1971, Zatka *et al.* reported the preparation of a tetradentate  $\beta$ -diketiminate ligand containing quinoline pendant arms.<sup>22</sup> Based on UV-vis spectroscopy, this ligand was found to form 1 : 1 complexes with Zn and Cd. Subsequent work has further established the affinity of quinoline ligands for Zn, giving complexes of high stability and high molar absorptivity values.<sup>23–26</sup>

In this work we describe the synthesis and characterization of a new tetradentate, monoanionic  $\beta$ -diketiminate ligand containing quinoline pendant donor groups that was prepared through the condensation of 2-(4-tolyl)-malondialdehyde and 8aminoquinoline. This ligand differs from that reported by Zatka *et al.* in that it bears a substituent on the central carbon of the BDI backbone. The new ligand, (BDI<sup>QQ</sup>)<sup>-</sup>, is shown in Fig. 1.



Fig. 1 Structure of tetradentate, monoanionic  $\beta$ -diketiminate ligand, (BDI<sup>QQ</sup>)<sup>-</sup>.

# Experimental

Chemicals that were purchased commercially and used without further purification include 2-(4-tolyl)malondialdehyde (Aldrich), 8-aminoquinoline (Aldrich), ethylmagnesium bromide (3 M solution in  $Et_2O$ , Aldrich), *p*-toluene sulfonic acid (Aldrich), and zinc(II) chloride (Mallinckrodt). Cadmium(II) acetate dihydrate (Aldrich) was dried with azeotropic distillation.

<sup>1</sup>H NMR spectra were acquired at 500 and 300 MHz, and <sup>13</sup>C NMR spectra were acquired at 75 MHz on Varian Inova Instruments. Positive polarity, electrospray ionization-time of flight (ESI-TOF) mass spectra were collected on a Bruker BioTOF II instrument. UV-vis absorbance spectra were collected with a Jasco V530 spectrophotometer (300–900 nm) with a 4 mL septumsealed quartz cuvette.

## Preparation of tetradentate $\beta$ -diketimine ligand

**2-(4-Tolyl)-1,3-bis(quinolyl)malondiimine,** (BDI<sup>QQ</sup>)H, (1). Compound 1 was prepared with two different methods for use as isolated material (Method A) and for reaction *in situ* (Method B) with transition metals. Method A: 8-aminoquinoline (400 mg, 2.81 mmol) and *p*-toluene sulfonic acid (33 mg, 0.20 mmol) were dissolved in 10 mL CHCl<sub>3</sub>, diluted into 125 mL toluene, and brought to reflux in an azeotropic distillation apparatus.

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2-(4-Tolyl)malondialdehyde (200 mg, 1.23 mmol) was dissolved in 10 mL CHCl<sub>3</sub> and added to the refluxing solution. The reaction solution was held at reflux for 1 h while H<sub>2</sub>O and CHCl<sub>3</sub> were removed from the system. The reaction solution was concentrated at elevated temperature to 60 mL. The reaction mixture was slowly cooled to -35 °C. Orange solids were isolated from the orange liquid with vacuum filtration. The ligand was neutralized and extracted with saturated NaHCO<sub>3</sub> solution and CHCl<sub>3</sub> at 0 °C, and the solvent was removed in vacuo, yield 46%. Method B: A similar reaction sequence was utilized with the following changes including 8-aminoquinoline as the limiting reagent. 8-Aminoquinoline (340 mg, 2.40 mmol) and p-toluene sulfonic acid (33 mg, 0.20 mmol) were dissolved in 10 mL CHCl<sub>3</sub>, diluted into 125 mL toluene, and brought to reflux in an azeotropic distillation apparatus. Then, 2-(4-tolyl)malondialdehyde (200 mg, 1.23 mmol) was dissolved in 10 mL CHCl<sub>3</sub> and added to the refluxing solution. The reaction solution was held at reflux for 1 h while  $H_2O$  and  $CHCl_3$  were removed from the system. The reaction solution was cooled to room temperature and used directly to prepare metal complexes. UV-Vis (THF):  $\lambda_{max}$  429, 741 nm. <sup>1</sup>H NMR ( $d_6$ -DMSO)  $\delta$  14.00 (t, J = 6.0 Hz, 1H); 8.83 (dd, J = 4.0, 2.0 Hz, 2H); 8.60 (d, J = 6.0 Hz, 2H); 8.38 (dd, J =8.0, 1.5 Hz, 2H); 7.84 (dd, J = 6.0, 3.0 Hz, 2H); 7,65 (m, 4H); 7.56 (dd, J = 4.0 Hz, 4H); 7.51 (d, J = 8.0 Hz, 2H); 7.22 (d, J =8.0 Hz, 2H); 2.33 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  156.85, 149.98, 138.77, 136.95, 132.15, 130.13, 129.15, 128.81, 128.02, 126.47, 125.49, 122.94, 115.23, 115.10, 21.91. ESI-TOF MS (MeOH): m/z observed: C<sub>28</sub>H<sub>23</sub>N<sub>4</sub>, [M + H]<sup>+</sup> = 415.3 m/z. ESI-TOF High resolution mass spectrometry (HRMS) with polypropylene glycol standard:  $C_{28}H_{23}N_4$ ,  $[M + H]^+ = 415.1916 m/z$ , 0.3 ppm error.

#### Preparation of tetradentate β-diketiminate metal complexes

2-(4-Tolyl)-1,3-bis(quinolyl)malondiiminate magnesium bromide, (BDI<sup>QQ</sup>)MgBr, (2). Under inert atmosphere, (BDI<sup>QQ</sup>)H (prepared with Method A, 40 mg, 0.10 mmol) was dissolved in toluene. In a separate vial, EtMgBr (100  $\mu$ L of a 3 M solution in Et<sub>2</sub>O, 0.30 mmol) was diluted in toluene. The ligand was added dropwise to the metal over 10 min with stirring. An immediate color change from the orange ligand and colorless magnesium solutions to a red metal complex solution was observed. The solids were isolated by glass fiber filter filtration, yield 24%. UV-Vis (THF):  $\lambda_{max}$  443, 549, 738 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  9.11 (dd, J = 5.0, 1.5 Hz, 2H); 8.78 (s, 2H); 8.48 (dd, *J* = 8.5, 1.5 Hz, 2H); 7.84 (d, *J* = 8.0 Hz, 2H); 7.73 (dd, J = 8.5, 5.0 Hz, 2H); 7.69 (t, J = 8.0 Hz, 2H); 7.61 (d, J = 8.0, 2H; 7.46 (d, J = 8.0, 2H); 7.25 (d, J = 8.0, 2H); 2.40 (s, 3H). ESI-TOF MS (MeOH): m/z observed:  $C_{28}H_{21}N_4Mg$ ,  $M^+ =$ 437.5. ESI-TOF High resolution mass spectrometry (HRMS) with polypropylene glycol standard:  $C_{28}H_{21}N_4Mg$ ,  $M^+ = 437.1628 m/z$ , -3.9 ppm error. X-Ray quality crystals were obtained by diffusion of hexanes into a saturated  $CH_2Cl_2$  solution (hexane :  $CH_2Cl_2$  (5 : 1)) under inert atmosphere.

**2-(4-Tolyl)-1,3-bis(quinolyl)malondiiminate** zinc(II) chloride, (**BDI**<sup>QQ</sup>)**ZnCl**, (3). Compound 3 was prepared in air by adding (BDI<sup>QQ</sup>)H (prepared with Method B, 8-aminoquinoline (360 mg, 2.53 mmol), *p*-toluene sulfonic acid (100 mg, 0.60 mmol), 2-(4-tolyl)malondialdehyde (215 mg, 1.33 mmol)) to a methanol solution of ZnCl<sub>2</sub> (200 mg, 1.47 mmol). The ligand solution was added to the metal over 1 h with stirring. An immediate color change from the orange ligand and colorless zinc chloride solutions to a red metal complex solution was observed. The solution was stirred overnight. Gold-colored solids were isolated by vacuum filtration with a glass fiber filter. Compound 3 was purified with recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and hexanes, 53% yield. UV-Vis (THF):  $\lambda_{max}$  559 nm ( $\epsilon = 8600 \text{ M}^{-1} \text{ cm}^{-1}$ ). <sup>1</sup>H NMR  $(CD_2Cl_2) \delta$  9.09 (d, J = 4.0 Hz, 2H); 8.79.50 (s, 2H); 8.45 (dd, J = 0.5, 8.0 Hz, 2H); 7.80 (d, J = 8.0 Hz, 2H); 7.72 (dd, J =2.0, 5.0 Hz, 2H); 7.68 (t, J = 8.0 Hz, 2H); 7.61 (d, J = 8.0 Hz, 2H); 7.46 (d, J = 8.0 Hz, 2H); 7.25 (d, J = 8.0 Hz, 2H); 2.40 (s, 3H) <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  154.78, 148.04, 144.25, 139.86, 135.47, 130.34, 129.88, 129.14, 127.05, 122.63, 121.74, 112.90, 112.39, 21.26. ESI-TOF MS (MeOH): m/z observed:  $C_{28}H_{21}N_4Zn$ ,  $M^+ =$ 477.2 m/z. ESI-TOF High resolution mass spectrometry (HRMS) with polypropylene glycol standard:  $C_{28}H_{21}N_4Zn$ ,  $M^+ = 477.0161$ m/z, -1.81 ppm error. X-Ray quality crystals were obtained by slow evaporation from a  $CH_2Cl_2$ : IPA (1 : 1) solution.

2-(4-Tolyl)-1,3-bis(quinolyl)malondiiminate cadmium(II) acetate, (BDI<sup>QQ</sup>)Cd(OAc), (4). Under inert atmosphere, (BDI<sup>QQ</sup>)H (prepared with Method A, 40 mg, 0.10 mmol) was dissolved in toluene. In a separate vial,  $Cd(OAc)_2$  (dried by azeotropic distillation, 30 mg, 0.13 mmol) was dissolved in THF. The ligand was added dropwise to the metal over 10 min with stirring. An immediate color change from the orange ligand and colorless cadmium solutions to a red metal complex solution was observed. A THF extraction was performed, and the solids were isolated by glass fiber filter filtration and washed with toluene, yield 11%. UV-Vis (THF):  $\lambda_{max}$  382, 455, 556 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  9.18 (<sup>1</sup>H–<sup>1</sup>H d, J = 4.0, <sup>111/113</sup>Cd–<sup>1</sup>H, d, <sup>3</sup>J = 1.0 Hz, 2H), 8.80 (<sup>111/113</sup>Cd–<sup>1</sup>H, t, <sup>3</sup>J =12.0 Hz, 2H, Cd coupling), 8.39 (dd, J = 8.0, 1.0 Hz, 2H); 7.69 (dd, J = 8.0, 4.0 Hz, 2H); 7.66 (d, J = 8.0 Hz, 2H); 7.65 (d, J = 5.0 Hz, 2H); 7.56 (d, J = 8.0, 2H); 7.49 (d, J = 8.0, 2H); 7.26 (d, J = 82H); 2.42 (s, 3H); 1.79 (s, 3H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ179.72, 156.76, 150.06, 145.36, 140.65, 140.50, 139.53, 135.11, 130.33, 129.76, 128.85, 127.21, 122.42, 121.46, 113.26, 22.22, 21.24. ESI-TOF MS (MeOH): m/z observed:  $C_{28}H_{21}N_4Cd$ ,  $M^+ = 527.2$ . ESI-TOF High resolution mass spectrometry (HRMS) with polypropylene glycol standard:  $C_{28}H_{21}N_4Cd$ ,  $M^+ = 527.0803 m/z$ , -1.6 ppm error. X-Ray quality crystals were obtained by diffusion of hexanes into a saturated  $CH_2Cl_2$  solution (hexane :  $CH_2Cl_2$  (5 : 1)).

**2-(4-Tolyl)-1-(quinolyl)malonimine-3-aldehyde, (BDI<sup>Q</sup>)OH, (5).** Compound **5** was isolated from two different recrystallizations of compound **1** in hexanes :  $CH_2Cl_2$  solutions. Yellow solids were isolated from the orange liquid with vacuum filtration. ESI-TOF MS (MeOH): m/z observed:  $C_{19}H_{17}N_2O_1$ ,  $[M + H]^+ = 289.3 m/z$ . ESI-TOF HRMS with polypropylene glycol standard:  $C_{19}H_{17}N_2O_1$ ,  $[M + H]^+ = 289.1345 m/z$ , -3.20 ppm error. X-Ray quality crystals were obtained by diffusion of hexanes into a saturated  $CH_2Cl_2$  solution (hexane :  $CH_2Cl_2$  (7 : 1)) and by diffusion of hexanes into a saturated  $CH_2Cl_2$  (4 : 1)).

#### Crystal structure determinations

Crystal data for compounds **2**, **3**, **4**, **5**, and **5**' were collected at 172(2) K using a Siemens SMART Platform CCD diffractometer.

	(BDI <sup>QQ</sup> )MgBr, 2	(BDIQQ)ZnCl, 3	(BDIQQ)Cd(OAc), 4	(BDI <sup>Q</sup> )OH, <b>5</b>	(BDI <sup>Q</sup> )OH, 5
Formula	C <sub>28</sub> H <sub>21</sub> Br Mg N <sub>4</sub>	C28 H21 Cl N4 Zn	C <sub>30</sub> H <sub>24</sub> Cd N <sub>4</sub> O <sub>2</sub>	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> O	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> O
MW	517.71	514.31	586.09	288.34	288.34
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1$	<i>P</i> -1	<i>P</i> -1	$P2_1$	P-1
a/Å	6.6796(12)	9.1946(13)	9.032(3)	11.4241(18)	6.3158(10)
b/Å	15.052(3)	10.9583(16)	12.744(4)	6.1370(10)	8.6984(14)
c/Å	11.681(2)	12.4820(18)	14.414(4)	11.8007(18)	13.841(2)
a/°	90	96.338(2)	113.725(3)	90	101.945(2)
β/°	91.041(3)	96.555(2)	104.610(3)	116.708(2)	91.645(3)
y/°	90	113.305(2)	95.018(3)	90	98.646(3)
$V/Å^3$	1174.2(4)	1130.7(3)	1435.9(7)	739.1(2)	734.1(2)
Ζ	2	2	2	2	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.464	1.511	1.549	1.296	1.304
$\mu/\text{mm}^{-1}$	1.802	1.230	0.982	0.081	0.082
F(000)	528	528	676	304	304
Crystal colour	red	Green-gold	Red	Orange	Orange
Ind. Reflns	4134	3984	5006	2613	3229
Obs. Reflns	3277	3530	4188	2242	2623
$R_{ m int}$	0.0513	0.0264	0.0311	0.0259	0.0217
GOOF on $F^2$	1.098	1.128	1.053	1.052	0.938
$R_1 \left[ I > 2\sigma(I) \right]$	0.0809	0.0375	0.0466	0.0326	0.0432
$WR_2 [I > 2\sigma(I)]$	0.2126	0.0750	0.1106	0.0740	0.1095

 $\label{eq:able_linear} \begin{array}{ll} \mbox{Table 1} & X-\mbox{Ray crystallographic data for (BDI^{QQ})} MgBr, (BDI^{QQ}) ZnCl, (BDI^{QQ}) Cd(OAc) \end{array}$ 

Data collection was carried out with Mo K $\alpha$  radiation (graphite monochromator) with a frame time of 30 s, 20 s, 90 s, 30 s, and 15 s for **2**, **3**, **4**, **5**, and **5**' respectively. Frames were collected with 0.30° steps in  $\omega$  at four different  $\phi$  settings and a detector position of  $-28^{\circ}$  in  $2\theta$ . The intensity data were corrected for adsorption and decay (SADABS).<sup>27</sup> The data was integrated with (SAINT).<sup>28</sup> The structures were solved using SHELXS-97 and refined using SHELXL-97.<sup>29</sup> Compound **2**, modeled as an inversion twin, contained a bisecting mirror plane of pseudosymmetry, requiring the use of 43 restraints to model the structure. Crystallographic data for compounds **2–5** are given in Table 1. Additional crystallographic data including tables of bond lengths and angles are presented in the ESI.<sup>†</sup>

CCDC reference numbers 612332-612336

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609616f

# **Results and discussion**

Compound 1 was prepared by the condensation of 2-(4-tolyl)malondialdehyde with 8-aminoquinoline and was isolated in 46% yield (eqn (1)).



Water generated in the reaction was removed by azeotropic distillation driving the equilibrium towards the products and avoiding ready hydrolysis of the imines generated in this reaction. Compound 1 was fully characterized with <sup>1</sup>H and <sup>13</sup>C NMR,

HRMS, and absorbance spectroscopy. The composition of **1** was confirmed by HRMS ESI-MS with polypropylene glycol exact mass internal standard. Compound **1** bonded irreversibly to chromatographic stationary phases and hydrolyzed during recrystallization. The semi-condensed compound, (BDI<sup>Q</sup>)OH, was characterized crystallographically in two different crystal systems, **5** and **5**'. Crystallographic data for these compounds is included in Table 1. ORTEP drawings are available in ESI.<sup>†</sup>



Compound **2**, (BDI<sup>QQ</sup>)MgBr, was prepared through the reaction of **1** and EtMgBr under inert atmosphere and isolated with vacuum filtration in 24% yield (eqn (2)).



Compound **2** was characterized by <sup>1</sup>H NMR spectroscopy, HRMS ESI-MS, absorbance spectroscopy, and X-ray crystallography. In the NMR spectroscopy, the spectrum showed highly resolved

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proton resonances with those closest to the metal appearing furthest downfield and the tolyl group appearing furthest upfield among the aromatic protons. Coupling constants were consistent with the ligand spectrum and the other metal complexes. During ESI-MS characterization, a signal for  $(C_{28}H_{21}N_4)Mg^+$  was observed at 437.5 m/z, and its composition was confirmed by HRMS ESI-MS with polypropylene glycol exact mass internal standard.

X-Ray quality crystals were isolated by slow diffusion of hexanes into a CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 2). The structure shows tetradentate equatorial coordination of the Mg center by the ligand with a fifth apical coordination site occupied by bromine, yielding a distorted square pyramidal geometry. Unfortunately, the structure is not of high enough quality to be useful for rigorous bond length and bond angle comparisons with other structures because the molecule is bisected by a mirror plane of pseudosymmetry. As a result, the canted quinolyl rings are reflected by pseudosymmetry from actual atom positions on one quinolyl ring to locations where the corresponding mirror image quinolyl atoms would be. This effect is also observed for the phenyl ring that is neither perpendicular nor parallel to the mirror of pseudosymmetry. As a result, the pseudosymmetry contributes to poor refinement values, large thermal parameters, and the use of many restraints to achieve planarity for the quinolyl and phenyl rings. We believe this contributes to the apparent "wagging" of the phenyl ring as well. See Table 2 for selected bond lengths of interest.



Fig. 2 ORTEP diagram of (BDI<sup>QQ</sup>)MgBr, 2, with thermal ellipsoids drawn at the 50% probability level.

Compound 3, (BDI<sup>QQ</sup>)ZnCl, was prepared with 1 prepared by Method B and  $ZnCl_2$  in air and was isolated in 53% yield (eqn (3)).



Compound **3** was characterized with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, HRMS ESI-MS, absorbance spectroscopy, and X-ray crystallography. Both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy show highly resolved quinolyl signals consistent with average mirror symmetry in the complex (Fig. 3). The coupling constants were similar to those observed in **1**. During ESI-MS characterization, a signal for ( $C_{28}H_{21}N_4$ )Zn<sup>+</sup> was observed at 477.2 *m/z* and had an isotope pattern consistent with Zn incorporation. The composition was confirmed by HRMS ESI-MS with polypropylene glycol internal exact mass standard. The absorbance spectrum shows an intense transition at 559 nm (Fig. 4).



Fig. 3 Downfield region of the <sup>1</sup>H NMR spectrum of (BDI<sup>QQ</sup>)ZnCl.

The X-ray crystal structure shows tetradentate equatorial coordination of the Zn center by (BDI<sup>QQ</sup>) with a fifth apical coordination site occupied by chlorine, yielding a distorted square

	Table 2	Bond lengths, dis	stances, and angles	of interest for (	BDI <sup>QQ</sup> )MgBr,	(BDI <sup>QQ</sup> )ZnCl,	(BDI <sup>QQ</sup> )Cd(C	)Ac)
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	(BDIQQ)MgBr, 2 <sup>a</sup>	(BDIQQ)ZnCl, 3	(BDIQQ)Cd(OAc), 4
M ionic radius/Å <sup>b</sup>	0.71	0.74	0.92
M–N1/M–N4 (quinolyl)/Å	$2.143(4)^{c}$	2.154(2)/2.161(2)	2.293(4)/2.315(4)
M-N2/M-N3 (iminate)/Å	$2.089(6)^{c}$	2.045(2)/2.071(2)	2.304(4)/2.281(4)
N1–N4/Å	3.314	3.335	3.808
N2–N3/Å	2.907	2.883	3.017
M–N4 plane/Å	0.5445	0.5202	0.6761
Q,Q plane twist/°	29.7	26.9	16.3
N2–M–N3 angle/°	88.2	88.9	82.3

<sup>*a*</sup> Data for **2** are from a lower quality structure and are shown only for trend comparison purposes. <sup>*b*</sup> Reference 30. <sup>*c*</sup> Equivalent bonds constrained to be the same length.



**Fig. 4** Absorbance spectrum of (BDI<sup>QQ</sup>)ZnCl, **3**, in THF with absorbance maximum at 559 nm.

pyramidal geometry (Fig. 5). There is a  $27^{\circ}$  twist angle between the quinolyl rings and the zinc center is located 0.52 Å above the N1–N2–N3–N4 plane. See Table 2 for other selected structural metrics.



Fig. 5 ORTEP diagram of  $(BDI^{QQ})ZnCl$ , 3, with thermal ellipsoids drawn at the 50% probability level.

Compound 4, (BDI<sup>QQ</sup>)Cd(OAc), was prepared through the reaction of 1 and Cd(OAc)<sub>2</sub> under an inert atmosphere and isolated by vacuum filtration in 11% yield (eqn (4)).



Compound 4 was characterized with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, HRMS ESI-MS, absorbance spectroscopy, and X-ray crystallography. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra showed highly resolved resonances (Fig. 6). During ESI-MS characterization, a signal for  $(C_{28}H_{21}N_4)Cd^+$  was observed at 527.2 *m/z* and had an isotope ratio indicative of Cd incorporation, and the composition



**Fig. 6** Downfield region of the <sup>1</sup>H NMR spectra of (BDI<sup>QQ</sup>)Cd(OAc). <sup>111/113</sup>Cd satellites are indicated with \*.

was confirmed by HRMS ESI-MS with polypropylene glycol internal standard.

X-Ray quality crystals were obtained by slow diffusion of hexanes into a  $CH_2Cl_2$  solution of **4** (Fig. 7). The structure shows tetradentate equatorial coordination of the Cd center by the BDI<sup>QQ</sup> ligand in addition to an acetate binding in an asymmetric bidentate manner. The result is a capped square pyramidal coordination geometry. Compound **4** contains a 16° twist angle between the quinolyl rings and the cadmium center is located 0.67 Å above the N1–N2–N3–N4 least squares plane. The acetate is in an intermediate coordination between unidentate and symmetric bidentate coordination (Cd–O1 2.276(4) Å and Cd–O2



Fig. 7 ORTEP diagram of (BDI<sup>QQ</sup>)Cd(OAc), 4, with thermal ellipsoids drawn at the 50% probability level. One molecule of  $CH_2Cl_2$  in the asymmetric unit is omitted for clarity.

2.610(4) Å) revealing a weak secondary interaction for Cd–O1. Further evidence of asymmetric coordination was revealed by comparison of the O1–Cd–N bond angles ( $100.7-110.83^{\circ}$ ) and O2–Cd–N bond angles (quinolyl  $81.1^{\circ}$  and  $81.2^{\circ}$  and iminate 132.7° and 137.6°). See Table 2 for selected additional metrics.

The structural features of the reported compounds reflect variations between central atom ionic radii and metal hardness. For example, Mg and Zn have very similar ionic radii, but Mg<sup>II</sup> is a hard metal center while Zn<sup>II</sup> is soft. In contrast, Zn<sup>II</sup> and Cd<sup>II</sup> have different sizes but have similar metal softness.<sup>30,31</sup>

### Spectroscopy of (BDIQQ)M complexes

The <sup>1</sup>H NMR spectroscopy indicates that the solution structures of the Mg, Zn, and Cd complexes all have average symmetric metal coordination between the two quinolyl moieties with no apparent fluctuations (Fig. 3 and 6). These results are consistent with the solid state structures. An interesting feature of the (BDI<sup>QQ</sup>)CdOAc <sup>1</sup>H NMR spectrum is the <sup>111/113</sup>Cd–<sup>1</sup>H coupling observed in the imine protons at 8.8 ppm of <sup>3</sup>*J* = 12 Hz (resonance g, Fig. 6). Similar coupling was observed between the cadmium and the  $\alpha$ -protons to the quinolyl nitrogen (9.2 ppm) observed as a doublet of doublets (resonance a, Fig. 6). The <sup>111</sup>Cd and <sup>113</sup>Cd satellites are not resolved from each other in these spectra due to their very similar gyromagnetic ratios, -5.6926 and  $-5.9550 \times 10^7$  rad T<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>32</sup>

The absorbance spectra of the (BDI<sup>QQ</sup>)M complexes **2**, **3**, and **4** show many similarities as expected for binding to closed shell spectroscopically silent metals. This is reflected in the observation of the absorbance maxima between 549 and 559 nm for the Mg, Zn, and Cd complexes. The spectroscopic properties are proposed to be ligand based  $\pi \rightarrow \pi^*$  transitions. Also, the molar absorptivities of the metal complexes were quite intense on the order of 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>. Similar molar absorptivity values for bis and tris 8-aminoquinoline complexes have been observed in this range.<sup>23,26</sup>

### Structures of (BDIQQ)M complexes

These reported structures join a rare group of acyclic tetradentate BDI ligands and are especially uncommon among nitrogen only donors. The structures of **2**, **3**, and **4** allow the opportunity to make comparisons to reported structures. A number of bidentate  $\beta$ -diketiminate structures of Zn and Mg compounds have been reported and their bond distances can be compared to complexes **2** and **3**.<sup>33–35</sup> The M–N2 and M–N3 bond distances in (BQI<sup>QQ</sup>)ZnCl are slightly longer than the reported bidentate compounds reflecting the effect of the quinolyl coordination drawing the metal away from the iminate nitrogen donors. Accordingly the N2–M–N3 bite angle is smaller for (BQI<sup>QQ</sup>)ZnCl (88.9°) than for the bidentate compounds (ranging from 94.4 to 97.0°) due to the increased M–iminate distance.<sup>33–35</sup> These trends are repeated for the (BQI<sup>QQ</sup>)Cd(OAc) and (BQI)CdI<sub>2</sub>Li(OEt<sub>2</sub>)<sub>2</sub> structures where the bite angles are 82.3° and 91.5°, respectively.<sup>34</sup>

One structure of particular interest for comparison is the *trans*-bis-(8-aminoquinoline)aquo zinc(II) tetrachlorozincate,  $[(8AQ)_2Zn(H_2O)][ZnCl_4]$ , structure which contains a fivecoordinate zinc ion.<sup>24</sup> The coordinate covalent bonds of the  $(8AQ)_2Zn(H_2O)$  quinoline rings are 0.040 Å shorter than in  $(BQI^{QQ})ZnCl.$  While the ionic nitrogen bonds are 0.30 Å longer in  $(8AQ)_2Zn(H_2O).^{24}$ 

For five-coordinate BDI complexes with pendant donor groups characterized here and elsewhere, the metal sits above the plane in a distorted square pyramidal geometry.<sup>16</sup> This stands in contrast to octahedral structures of Sc and Fe with pendant donors. In these examples, the metal sits in the plane of the equatorial BDI ligand.<sup>18,20</sup>

There are several comparisons that can be made between the Mg, Zn, and Cd structures (Table 2).

Among their similarities, all structures show the BDI<sup>QQ</sup> ligand in an equatorial position. It appears that the BDI<sup>QQ</sup> ligand is sufficiently rigid as to force equatorial coordination. This is most clearly seen in the six-coordinate (BDI<sup>QQ</sup>)Cd(OAc) structure, which adopts an unusual capped square pyramidal geometry. However, the ligand is flexible enough to accommodate different metal center radii as revealed by the N1–N4 interatomic through space distances for the Zn and Cd structures which is 0.473 Å greater in (BDI<sup>QQ</sup>)Cd(OAc), resulting from the larger Cd ionic radius and minimizing quinolyl C–H steric interactions. Varying ligand pocket size has been recently reported for complexes with pendant quinolyl donors.<sup>4</sup>

# Conclusions

This work represents a significant step into the development of acyclic monoanionic tetradentate nitrogen ligands using the  $\beta$ -diketiminate platform. We have shown that the ligand can be readily prepared and metal complexes of Mg, Zn, and Cd can be prepared. We believe this ligand has promise in modeling the monoanionic tetraaza core found in the biologically relevant metal-containing cofactors, vitamin B<sub>12</sub> and F<sub>430</sub>. Experiments testing this idea are in progress.

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