## Syntheses, structures, and photophysical properties of Zn<sup>II</sup> and Cd<sup>II</sup> metal complexes based on benzoylhydrazones\*

E. V. Nosova,<sup>a\*</sup> A. A. Chupakhin,<sup>a</sup> G. N. Lipunova,<sup>a,b</sup> P. A. Slepukhin,<sup>a,b</sup> M. S. Valova,<sup>b</sup> and V. N. Charushin<sup>a,b</sup>

<sup>a</sup>Ural Federal University named after the First President of Russia B. N. Yeltsin, 19 ul. Mira, 620002 Ekaterinburg, Russian Federation. E-mail: emily74@rambler.ru <sup>b</sup>I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,

22 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation.

E-mail: lipunova@ios.uran.ru

Novel ligands were synthesized by the reaction of benzazine-2-carbaldehydes or methyl pyrazinyl ketone with benzhydrazide, as well as their Zn<sup>II</sup> and Cd<sup>II</sup> complexes with the N,N,O environment. Their structures and photophysical properties were studied. The synthesized complexes are photoluminescent.

**Key words**: 6,7-difluoroquinoline-2-carbaldehyde, quinoxaline-2-carbaldehyde, 2-acetylpyrazine, benzoylhydrazones, zinc(11) complexes, cadmium(11) complexes, photoluminescence.

In the production of electroluminescent materials, increased attention is recently given to ligands capable of forming individual lanthanide complexes with the N,N,O, O,N,O, O,N,N,O, or O,N,N,N environment, which are promising emitters in the visible and near-IR spectral ranges.<sup>1–4</sup> The known ligands of this type are mainly presented by 8-hydroxyquinoline derivatives containing in position 2 pyridin-2-yl, benzazol-2-yl, amide, azomethine, or hydrazone fragments.<sup>5,6</sup> Lanthanide complexes formed by them can be either mono- or binuclear depending on the nature of the substituent in position 2 of quinoline and synthesis conditions.<sup>6–10</sup> 8-Hydroxyquinoline derivatives with the N-donor fragment in position 2 are widely used as ligands for lanthanide complexes and for complexes with other metals with the N,N,O environment, and their unusual properties were revealed. For example, 2-(pyridin-2-yl)-8-hydroxyquinoline can stabilize the high oxidation state of nickel and cobalt and different oxidation states of copper in the complexes.<sup>11</sup> The dinaphthyl derivative of 8-carboxamidoquinoline, which is also capable of forming complexes with the N,N,O environment of the metal, was described as an efficient sensor for the determination of Zn<sup>II</sup> and Cu<sup>II</sup> due to fluorescence enhancement or quenching.<sup>12</sup> The data on the formation of complexes with the N,N,O environment of the metal based on quinoline derivatives containing no O- and N-donor substituents in position 8 are restricted.13

We have previously proposed novel ligands with the N,N,O environment, *viz.*, 2-hydroxybenzaldehyde (2-phen-

ylquinazolin-4-yl)hydrazones, obtained their complexes with  $zinc(\pi)$ , and studied the photophysical properties of the ligand and complexes.<sup>14</sup>

In this work we synthesized benzoylhydrazones of benzazine-2-carboxaldehydes 3a-c (quinoline-2-carboxaldehyde, 6,7-difluoroquinoline-2-carboxaldehyde, and quinoxaline-2-carboxaldehyde), as well as methyl pyrazinyl ketone benzoylhydrazone 5, and Zn<sup>II</sup> and Cd<sup>II</sup> complexes 6 and 7 based on these ligands. Ligand 5 has earlier been described<sup>15</sup> as an efficient chemosensor to aluminum cation, and the 1: 1 complex is formed without the substitution of the proton of the ligand. We assumed that on heating ligand 5 with zinc and cadmium salts would produce 2:1 metal complexes; in addition, we intended to analyze the properties of compound 5 in comparison with its benzo analog, quinoxaline derivative 3c. The presence of the fluorine atom in molecule 3b could increase both the thermal and chemical stability and solubility in organic solvents, which is necessary for the improvement of the quality of the films.<sup>16</sup>

Reflux of benzhydrazide 1 with quinoline(quinoxaline)-2-carbaldehydes 2 in ethanol gave the corresponding hydrazones 3 (Scheme 1). Complexes of  $Zn^{II}$  and  $Cd^{II}$ **6a,c,d** and 7 were synthesized by heating hydrazones 3 and 5 with zinc acetate in a mole ratio of 2 : 1 in DMF in the absence of a base or with cadmium iodide in the presence of sodium hydroxide for 3 h. More drastic conditions were required for the synthesis of the  $Zn^{II}$  complex based on difluoroquinoline derivative **3b**, namely, heating of **3b** with  $Zn(OAc)_2 \cdot 2H_2O$  in a mole ratio of 2 : 1 in DMF at 150 °C for 10 h. However, under these conditions both complex formation and substitution of the

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F(7) atom for the dimethylamino group (compound **6b**). The <sup>1</sup>H NMR spectra of complexes **6** and **7** exhibits no signal from the NH group, and the shift of the signals from the CH=N group and protons of the pyridine (pyr-azine) cycle compared to the signals from the ligands is observed.



**2**, **3**: X = CH, Y = H (**a**), F (**b**); X = N, Y = H (**c**)

6	М	х	Y	Z
а	Zn	СН	Н	Н
b	Zn	СН	F	NMe <sub>2</sub>
С	Zn	Ν	Н	н
d	Cd	Ν	Н	Н

7: M = Zn (a), Cd (b)

**Reagents and conditions:** *i*.  $Zn(OAc)_2$ , DMF or CdI<sub>2</sub>, NaOH, EtOH.

According to the data of mass spectrometry, zinc complexes 6a-c and 7a have the composition  $L_2M$ . The elemental analysis data of the zinc and cadmium complexes also correspond to this composition. The structure of complex 6b was determined by X-ray diffraction analysis (Fig. 1).

According to the X-ray diffraction data, molecules of the complex in crystal are localized in the general position of the centrosymmetric space group. The mononuclear complex has a standard distorted octahedral environment of the central atom with a scatter of metal-heteroatom bond lengths of 2.05–2.28 Å (see Fig. 1, Table 1). The organic molecules act as tridentate ligands closing two five-membered metallocycles on the central atom. The non-hydrogen atoms of the ligand are arranged approximately in one plane, and the planes of the ligands are nearly orthogonal (the dihedral angle between the planes passing through atoms of the nearest coordination environment of the central atom is 89.0°). The bond lengths of atoms of the second period are equalized to a considerable extent, and a distinct difference between bonds of different types is observed in the metalloheterocycle involving the quinoline fragment. The molecular packing includes the solvate moiety. The solvent atoms are characterized by the very high values of thermal parameters, their point localization is impossible, and their contribution to the structural model was taken into account by the SQUEEZE procedure of the PLATON program.

There are no pronounced  $\pi$ -stacking interactions in the crystalline packing. In particular, the minimum interatomic distance between the non-hydrogen atoms of the peripheral phenyl substituent and quinoline fragment of the molecule [-x, 1-y, 1-z] exceeds 3.5 Å (Fig. 2). The interatomic distances between the edges of the p-systems involved in chelation are somewhat shorter and attain 2.91 Å for the pair of atoms N(3)…C(4) [-x, 2-y, 1-z] (Fig. 3), but the efficient overlapping of the p-systems of the complexes seems improbable in this case.

Hydrazones 3 and 5 are characterized by the longwavelength band in the absorption spectra in the range 298-343 nm, and their complexes 6 and 7 exhibit the band at 391-447 nm (Table 2). On going from the ligand of the pyrazine series (5) to the ligands of the benzazine series (3), the bathochromic shift of the long-wavelength absorption band (LWAB). The transition from the ligand

Table 1. Selected bond lengths in compound 6b

Bond	d/Å	Bond	d∕Å
Zn(1)-O(1)	2.191(3)	Zn(1) - O(2)	2.192(2)
Zn(1) - N(1)	2.199(3)	Zn(1) - N(5)	2.283(3)
Zn(1) - N(2)	2.066(3)	Zn(1) - N(6)	2.049(3)
O(1) - C(13)	1.263(4)	O(2)-C(32)	1.258(4)
N(1) - C(2)	1.337(4)	N(5)-C(21)	1.329(4)
N(1)-C(10)	1.384(5)	N(5)-C(29)	1.374(4)



Fig. 1. Structure of complex 6b according to the X-ray diffraction data in thermal ellipsoids of 50% probability.

to complex, is accompanied by the bathochromic shift of the LWAB by 69–108 nm in all cases (see Table 2).

The study of photolumienscence in an acetonitrile solution at room temperature revealed that hydrazones 3aand 5 exhibited no luminescence properties. However, the transition from quinoline derivative 3a to quinoxaline derivative 3c or from pyrazine derivative 5 to quinoxaline derivative 3c, as well as the presence of fluorine atoms in the quinoline fragment (3b) results in the appearance of blue photoluminescence (see Table 2). Complexes 6 and 7exhibit green, yellow-green, or yellow-orange luminescence with an emission maximum at 508-568 nm and have a high Stokes shift (96-175 nm). The emission maximum in the spectrum of disubstituted complex 6b is shifted to the red region by 60 nm compared to the spectrum of unsubstituted analog 6a. Cadmium complexes 6d and 7bluminesce in a longer-wavelength region than zinc complexes **6a** and **7a** (see Table 2). The photoluminescence intensity is determined by the ligand structure and other factors. The luminescence quantum yield of quinoxaline



Fig. 2. Fragment of the packing of complex 6b.



Fig. 3. Interatomic distances in the packing of complex 6b.



**Fig. 4.** Absorption (1), excitation (2), and fluorescence (3) spectra of a solution of compound **6b** in acetonitrile.

hydrazone **3c** is almost by two orders of magnitude higher than that for disubstituted quinoline derivative **3b**. At the same time, the transition from ligand **3b** to its complex **6b** is accompanied by a significant increase in the quantum



**Fig. 5.** Absorption (1, 2) and fluorescence (3, 50-fold amplified; (4) spectra of a solution of compound **6c** in acetonitrile (1, 3) and in the polycrystalline film (2, 4).

yield (see Table 2, Fig. 4), whereas for quinoxaline hydrazone **3c** the transition to complexes **6c** and **6d** is characterized by so strong decrease that we failed to determine it for complex **6c**. It should be mentioned that in the polycrystalline film complexes **6c** and **6d** have intensive yellow-orange luminescence (see Table 2, Fig. 5).

Thus, the novel complexes with the N,N,O environment of the metal and octahedral structure were synthesized and have photoluminescence in solutions and in the polycrystalline film. The possibility of tuning the fluorescence color and a high Stokes shift make these compounds promising for further studies.

## **Experimental**

<sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> were recorded on a Bruker DRX-400 spectrometer with a working frequency of 400.13 MHz, and chemical shifts were measured relatively to  $SiMe_4$  (<sup>1</sup>H).

Com- pound	Absorption, $\lambda_{max}/nm$	Photoluminescence		Stokes	Quantum
		Excitation, $\lambda_{max}/nm$	Emission, $\lambda_{max}/nm$	shift, Δλ/nm	yield, φ
3a	343, 329, 315, 307	_	_	_	_
3b	343, 329, 312, 301	343	366	37	$3.2 \cdot 10^{-5}$
3c	339, 317, 307	339	419	85	$2.7 \cdot 10^{-3}$
5	298	_	_	_	_
6a	412, 343, 307	412	508	96	$3.2 \cdot 10^{-5}$
6b	442, 379, 305 sh	442	568	120	$5.4 \cdot 10^{-2}$
6c	438, 315	315	552 (564)*	114(109)*	_
6d	447, 315, 288	447	555 (575)*	108(96)*	$2.8 \cdot 10^{-5}$
7a	391, 311	391	546	153	$5 \cdot 10^{-4}$
7b	393, 307	393	568	175	$1 \cdot 10^{-4}$

Table 2. Absorption and photoluminescence spectra data for benzoylhydrazones 3 and 5 and complexes 6 and 7 in acetonitrile at 293 K

\* Polycrystalline film.

<sup>19</sup>F NMR spectra were detected on a Bruker Avance 400 spectrometer with a working frequency of 376.43 MHz, and chemical shifts were measured relatively to CFCl<sub>3</sub> using C<sub>6</sub>F<sub>6</sub> as a secondary standard ( $\delta$ (<sup>19</sup>F) –162.9). Mass spectra were recorded on a SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. UV and FL spectra were obtained on a Shimadzu UV-2401PC spectrophotometer (Japan) and a Varian Eclipse spectrofluorimeter (Australia), and solutions in acetonitrile with a concentration of 10<sup>-4</sup> mol L<sup>-1</sup> were used for spectra recording. The relative quantum yield was determined using a known procedure<sup>17</sup> using quinine bisulfate ( $\varphi = 0.546$ ) and fluorescein for compound **6d** ( $\varphi = 0.92$ ) as standards.

X-ray diffraction study of compound 6b was carried out on an Xcalibur S automated X-ray diffractometer using a standard procedure ( $\lambda$ MoK $\alpha$  = 0.71073 Å, T = 295(2) K,  $\omega$  scan mode with an increment of 1° and a crystal-detector distance of 50 mm). The number of reflections collected on the scattering angles  $1.64 < \theta < 26.37^{\circ}$  was 13 707, of which 7334 reflections were independent ( $R_{int} = 0.0452$ ), and 4516 reflections were with  $I > 2\sigma(I)$ . An empirical absorption correction was applied  $(\mu = 0.722 \text{ mm}^{-1})$ . The crystal was triclinic, space group  $P\overline{1}$ , a = 11.3242(5) Å, b = 13.0648(9) Å, c = 14.1811(8) Å,  $\alpha = 116.518(6)^{\circ}, \beta = 99.331(4)^{\circ}, \gamma = 91.845(4)^{\circ}.$  The structure was solved by a direct method and refined in the anisotropic approximation using the SHELXTL program package.<sup>18</sup> The parameters of the final refinement were  $R^1 = 0.0611$ ,  $wR^2 =$ = 0.1512 for reflections with  $I > 2\sigma(I)$  at the goodness-of-fit S = 1.002. The maximum and minimum of the residual electron density were 0.556 and -0.494 e Å<sup>-3</sup>.

The results of X-ray diffraction analyses for compound **6b** were deposited with the Cambridge Crystallographic Data Centre (CCDC 1000078). These data are free and can be available at www.ccdc.cam.ac.uk.

Melting points were determined on a Stuart SMP3 instrument.

2-Formylbenzazines 2a-c were synthesized by the oxidation of the corresponding 2-methyl derivatives by selenium dioxide on reflux in dioxane.<sup>19</sup> Ligand 5 was synthesized by reflux of benzhydrazide 1 with 2-acetylpyrazine 4 in ethanol according to a described procedure.<sup>15</sup>

Benzoic acid (quinoxalin-2-yl)methylenehydrazide (3c). A solution of benzhydrazide (1) (0.172 g, 1.27 mmol) in ethanol (15 mL) was added to a solution of quinoxaline-2-carbaldehyde (2c) (0.2 g, 1.27 mmol) in ethanol (25 mL). The reaction mixture was refluxed for 10 h, then the solvent was distilled off to 1/4 volume, and the formed precipitate was filtered off. The yield was 0.31 g (89%), m.p. 224–226 °C. <sup>1</sup>H NMR,  $\delta$ : 7.55 (m, 2 H); 7.61 (m, 1 H); 7.84 (m, 2 H); 7.98 (m, 2 H); 8.10 (m, 2 H); 8.66 (s, 1 H, H(3)); 9.55 (s, 1 H, CH=N); 12.2 (br.s, 1 H, NH). Found (%): C, 69.61; H, 4.44; N, 20.22. C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>O. Calculated (%): C, 69.55; H, 4.38; N, 20.28.

Compounds **3a**,**b** were synthesized similarly.

**Benzoic acid (quinolin-2-yl)methylenehydrazide (3a).** The yield was 84%, m.p. 140–142 °C. <sup>1</sup>H NMR,  $\delta$ : 7.5–7.6 (m, 4 H); 7.75 (m, 1 H); 7.95 (m, 3 H); 8.03 (m, 1 H); 8.21 (m, 1 H, H(3)); 8.30 (m, 1 H, H(4)); 8.60 (s, 1 H, CH=N); 12.0 (br.s, 1 H, NH). Found (%): C, 74.13; H, 4.71; N, 15.32. C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>O. Calculated (%): C, 74.17; H, 4.76; N, 15.26.

**Benzoic acid (6,7-difluoroquinolin-2-yl)methylenehydrazide** (**3b).** The yield was 87%, m.p. 246–248 °C. <sup>1</sup>H NMR,  $\delta$ : 7.5–7.6 (m, 3 H); 7.9–8.0 (m, 4 H); 8.24 (d, 1 H, H(3), J=8.3 Hz); 8.39 (d, 1 H, H(4), J = 8.3 Hz); 8.59 (s, 1 H, CH=N); 12.1 (br.s, 1 H, NH). <sup>19</sup>F{<sup>1</sup>H} NMR,  $\delta$ : -135.49 (d, 1 F, F(7), J = 21.3 Hz); -132.26 (d, 1 F, F(6), J = 21.3 Hz). MS, m/z ( $I_{rel}$  (%)): 311 [M]<sup>+</sup> (3), 206 [M-C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (86), 178 [M-C<sub>6</sub>H<sub>5</sub>CO-N<sub>2</sub>]<sup>+</sup> (41), 151 (35), 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (100), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (66). Found (%): C, 65.54; H, 3.52; N, 13.57. C<sub>17</sub>H<sub>11</sub>F<sub>2</sub>N<sub>3</sub>O. Calculated (%): C, 65.59; H, 3.56; N, 13.50.

**Methyl pyrazinyl ketone benzoylhydrazone (5).** The melting point corresponds to the literature data.<sup>15 1</sup>H NMR,  $\delta$ : 2.47 (s, 3 H, Me); 7.5–7.8 (m, 3 H, H(3'), H(4'), H(5')); 7.97 (m, 2 H, H(2'), H(6')), 8.54 (m, 2 H, H(5), H(6)); 9.32 (d, 1 H, H(3), J = 1.3 Hz); 10.9 (br.s, 1 H, NH).

Zinc(II) complex of benzoic acid (quinolin-2-yl)methylenehydrazide (6a). A solution of zinc acetate dihydrate (0.084 g, 0.365 mmol) in water (3 mL) was added dropwise to hydrazone **3a** (0.2 g, 0.73 mmol) in freshly distilled DMF (15 mL). The reaction mixture was refluxed for 3 h and cooled, and the bright yellow precipitate was filtered off and washed with ethanol. The yield was 0.15 g (67%), m.p. >300 °C. <sup>1</sup>H NMR, δ: 7.32 (m, 2 H); 7.39 (m, 1 H); 7.45 (m, 1 H); 7.54 (m, 1 H); 7.57 (m, 1 H); 7.90 (m, 1 H); 8.0—8.15 (m, 3 H); 8.58 (d, 1 H, H(4), J = 8.4 Hz); 9.03 (s, 1 H, CH=N). MS, m/z ( $I_{rel}$  (%)): 614 [M]<sup>+</sup> (3), 457 (10), 170 (19), 142 (14), 128 (19), 115 (22), 105 (100), 77 (91). Found (%): C, 66.43; H, 3.81; N, 13.59. C<sub>34</sub>H<sub>24</sub>N<sub>6</sub>O<sub>2</sub>Zn. Calculated (%): C, 66.51; H, 3.94; N, 13.69. The molecular weight was 613.98.

Compounds **6b**, **c** and **7a** were synthesized similarly. To obtain complex **6b**, the reaction mixture was heated at 150 °C for 10 h, cooled, and filtered. The solution was slowly evaporated at room temperature, and the precipitated orange crystals were filtered off and used directly for X-ray diffraction analysis.

**Zinc(II) complex of benzoic acid [6-fluoro-7-(dimethylamino)quinolin-2-yl]methylenehydrazide (6b).** The yield was 59%, m.p. >300 °C. <sup>1</sup>H NMR, δ: 2.88 (s, 6 H, NMe<sub>2</sub>); 6.76 (d, 1 H, H(8), J = 8.6 Hz); 7.33 (m, 2 H, Ph); 7.36 (m, 1 H, Ph); 7.48 (d, 1 H, H(5), J = 14.0 Hz); 7.69 (d, 1 H, H(3), J = 8.3 Hz); 8.09 (m, 2 H, Ph); 8.29 (d, 1 H, H(4), J = 8.3 Hz); 8.87 (s, 1 H, CH=N). <sup>19</sup>F{<sup>1</sup>H} NMR, δ: -118.28 (c, 1 F). MS, m/z ( $I_{rel}$  (%)): 736 [M]<sup>+</sup> (4), 247 (15), 246 (19), 242 (11), 217 (10), 215 (31), 214 (15), 203 (10), 189 (10), 188 (11), 121 (18), 111 (17), 106 (14), 105 (100), 103 (34), 97 (16), 77 (68). Found (%): C, 61.95; H, 4.31; N, 15.29. C<sub>38</sub>H<sub>32</sub>F<sub>2</sub>N<sub>8</sub>O<sub>2</sub>Zn. Calculated (%): C, 62.01; H, 4.38; N, 15.22. The molecular weight was 736.10.

Zinc(II) complex of benzoic acid (quinoxalin-2-yl)methylenehydrazide (6c). The yield was 69%, m.p. >300 °C. <sup>1</sup>H NMR,  $\delta$ : 7.41 (m, 2 H); 7.45 (m, 1 H); 7.64 (m, 1 H); 7.71 (m, 2 H); 8.00 (m, 1 H); 8.13 (m, 1 H); 8.15 (m, 1 H); 9.17 (s, 1 H, H(3)); 9.39 (s, 1 H, CH=N). MS, m/z ( $I_{rel}$  (%)): 616 [M]<sup>+</sup> (4), 614 (5), 458 (5), 155 (8), 130 (5), 129 (11), 105 (100), 103 (40), 77 (88). Found (%): C, 62.08; H, 3.78; N, 18.43. C<sub>32</sub>H<sub>22</sub>N<sub>8</sub>O<sub>2</sub>Zn. Calculated (%): C, 62.40; H, 3.60; N, 18.19. The molecular weight was 615.95.

Zinc(II) complex of benzoic acid (1-pyrazin-2-yl)ethylidenehydrazide (7a). The yield was 76%, m.p. >300 °C. <sup>1</sup>H NMR,  $\delta$ : 2.90 (s, 3 H, Me); 7.40–7.48 (m, 3 H, H(3'), H(4'), H(5')); 7.93 (m, 1 H, H(6')); 8.15 (m, 2 H, H(5), H(6)); 8.68 (m, 1 H, H(2')); 9.26 (d, 1 H, H(3), J = 1.3 Hz). MS, m/z ( $I_{rel}$  (%)): 544 [M]<sup>+</sup> (30), 527 (13), 307 (18), 305 (25), 303 (42), 106 (15), 105 (100), 93 (11), 79 (39), 77 (52). Found (%): C, 57.34; H, 4.12; N, 20.51. C<sub>26</sub>H<sub>22</sub>N<sub>8</sub>O<sub>2</sub>Zn. Calculated (%): C, 57.42; H, 4.08; N, 20.60. The molecular weight was 543.89. Cadmium(II) complex of benzoic acid (1-pyrazin-2-yl)ethylidenehydrazide (7b). A solution of sodium hydroxide (0.024 g, 0.6 mmol) in water (2 mL) was added to ligand 1 (0.15 g, 0.62 mmol) in ethanol (20 mL). A suspension of cadmium iodide (0.055 g, 0.31 mmol) in water (3 mL) was added to the obtained bright yellow solution. The reaction mixture was refluxed for 3 h, and the precipitate formed after cooling was filtered off and washed with diethyl ether. The yield was 0.168 g (92%), m.p. >300 °C. <sup>1</sup>H NMR,  $\delta$ : 2.85 (s, 3 H, Me); 7.38–7.44 (m, 3 H, H(3'), H(4'), H(5')); 8.03 (m, 1 H, H(6')); 8.22 (m, 2 H, H(5), H(6)); 8.65 (m, 1 H, H(2')); 9.18 (d, 1 H, H(3), J = 1.3 Hz). Found (%): C, 52.77; H, 3.82; N, 18.88. C<sub>26</sub>H<sub>22</sub>CdN<sub>8</sub>O<sub>2</sub>. Calculated (%): C, 52.85; H, 3.75; N, 18.96. The molecular weight was 590.92.

Compound 6d was synthesized similarly.

Cadmium(II) complex of benzoic acid (quinoxalin-2-yl)methylenehydrazide (6d). The yield was 64%, m.p.  $>300 \,^{\circ}$ C. <sup>1</sup>H NMR, &: 7.40 (m, 2 H); 7.46 (m, 1 H); 7.66 (m, 1 H); 7.74 (m, 2 H); &.05 (m, 1 H); &.16 (m, 2 H); 9.07 (s, 1 H, H(3)); 9.33 (s, 1 H, CH=N). Found (%): C, 58.24; H, 3.05; N, 17.28. C<sub>32</sub>H<sub>22</sub>CdN<sub>8</sub>O<sub>2</sub>. Calculated (%): C, 57.97; H, 3.34; N, 16.90. The molecular weight was 662.98.

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