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Spectral and Theoretical Study of 2-Methyl-3-{[(*Z*)-3-methyl-5-oxo-1-phenylpyrazol-4-ylidene)methyl]amino}quinazolin-4-one and Its Complexes with Metal Ions M(II)

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Abstract—2-Methyl-3-{[(*Z*)-3-methyl-5-oxo-1-phenylpyrazol-4-ylidene)methyl]amino}quinazolin-4-one was synthesized by condensation of 5-hydroxy-4-formyl-3-methyl-1-phenylpyrazole with N-amino-2-methylquinazolin-4-one and its structure and properties were studied by IR, ^{1}H, ^{13}C NMR, 2D ^{1}H NMR (COSY) and electronic spectroscopy and mass-spectrometry. By the reaction of compound (III) with Cd(II), Zn(II), and Pb(II) acetates the intracomplex compounds of 1 : 2 composition (metal : ligand) were obtained.

Keywords: enamines, NMR spectroscopy, electron spectroscopy, quantum-chemical calculations

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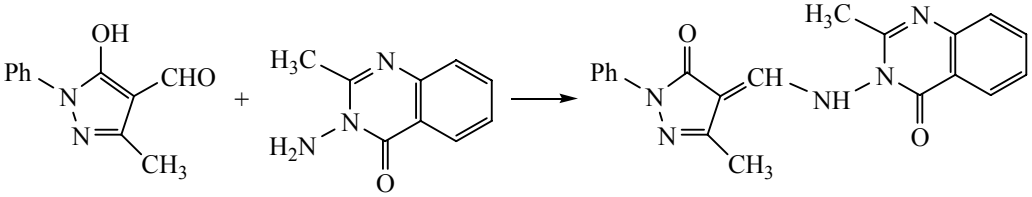
The products of condensation of *N*-aminoquinazolinones with carbonyl compounds, azomethines and enamines, attract the interest first of all due to their diverse and pronounced biological activity [1]. Among them, there are compounds with antibacterial [2], antimicrobial, antifungal activity [3], etc. On the other hand, the pyrazolone derivatives also belong to biologically active compounds [4]. In particular, they possess antifungal [5], tuberculocidal [6], antidiabetic [7], and other types of activity. Besides, the derivatives of *N*-aminoquinazolinones are known to possess high complexing ability [8–11].

In continuation of our studies on tautomerism and complexing ability of azomethines based on hydroxypyrazole [12, 13], in this work we have synthesized compound **III** (Scheme 1).

The product of condensation of 5-hydroxy-4-formyl-3-methyl-1-phenylpyrazole with *N*-amino-2-methylquinazolin-4-one can exist in various tautomeric forms, the most preferable being those where an intramolecular hydrogen bond can be realized.

In order to elucidate the pattern of coordination of the hydrogen atom forming the hydrogen bonds we

Scheme 1.



I **II** **III**

Table 1. Total (E, a.u.) and relative (ΔE, kcal/mol) energies of conformers **A** and **B** in gas phase and solutions. Most stable conformers with ($\mathbf{A_1}$, $\mathbf{B_1}$) and without intramolecular hydrogen bond ($\mathbf{A_2}$, $\mathbf{B_2}$) are given

System	Gas		DMSO		Methanol		Chloroform	
	E	ΔE	E	ΔE	E	ΔE	E	ΔE
$\mathbf{A_1}$	–1196.59582	1.9	–1196.60783	4.3	–1196.60761	4.3	–1196.60404	3.6
$\mathbf{A_2}$	–1196.58244	10.3	–1196.59673	11.3	–1196.59668	11.2	–1196.59214	11.0
$\mathbf{B_1}$	–1196.59880	0.0	–1196.61476	0.0	–1196.61446	0.0	–1196.60970	0.0
$\mathbf{B_2}$	–1196.58863	6.4	–1196.60755	4.5	–1196.60719	4.6	–1196.60137	5.2

have performed quantum-chemical calculations at the B3LYP/6-31G** level [14–16] using Gaussian-03 software [17]. The calculated energy and geometric characteristics of the OH- (**A**) and NH-forms (**B**) corresponding to the minima on the potential energy surface (PES) are presented in Table 1 and Fig. 1. As follows from calculations, in all studied media the NH-form (**B**) is more stable. All conformers in all media are nonplanar. Thus, structures $\mathbf{A_1}$ and $\mathbf{B_1}$ in gas phase are characterized by the angle between the phenyl and pyrazolone fragments of ca. 25º, and between the enamine and quinazolinone fragments, of 45º.

The difference of the total energies of conformers **A** and **B** with and without the intramolecular hydrogen bond determines the strength of this bond, which, for example, in DMSO is equal to 7.0 and 4.5 kcal/mol respectively (Table 1).

Isomers **A** and **B** form dimers of $\mathbf{C_2}$ symmetry with two intermolecular hydrogen bonds. A similar effect was found earlier for 3-[4-(dimethylamino)benzylideneamino]-2-methylquinazolin-4(3*H*)-one [18]. For example, for system **A** the energy of stabilization of the dimer relative to the most stable monomeric form $\mathbf{B_1}$ is 3.1 kcal/mol (Fig. 2).

Results of calculations are in agreement with the data of ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum of quinazolinone **III** in DMSO-d_6 contains

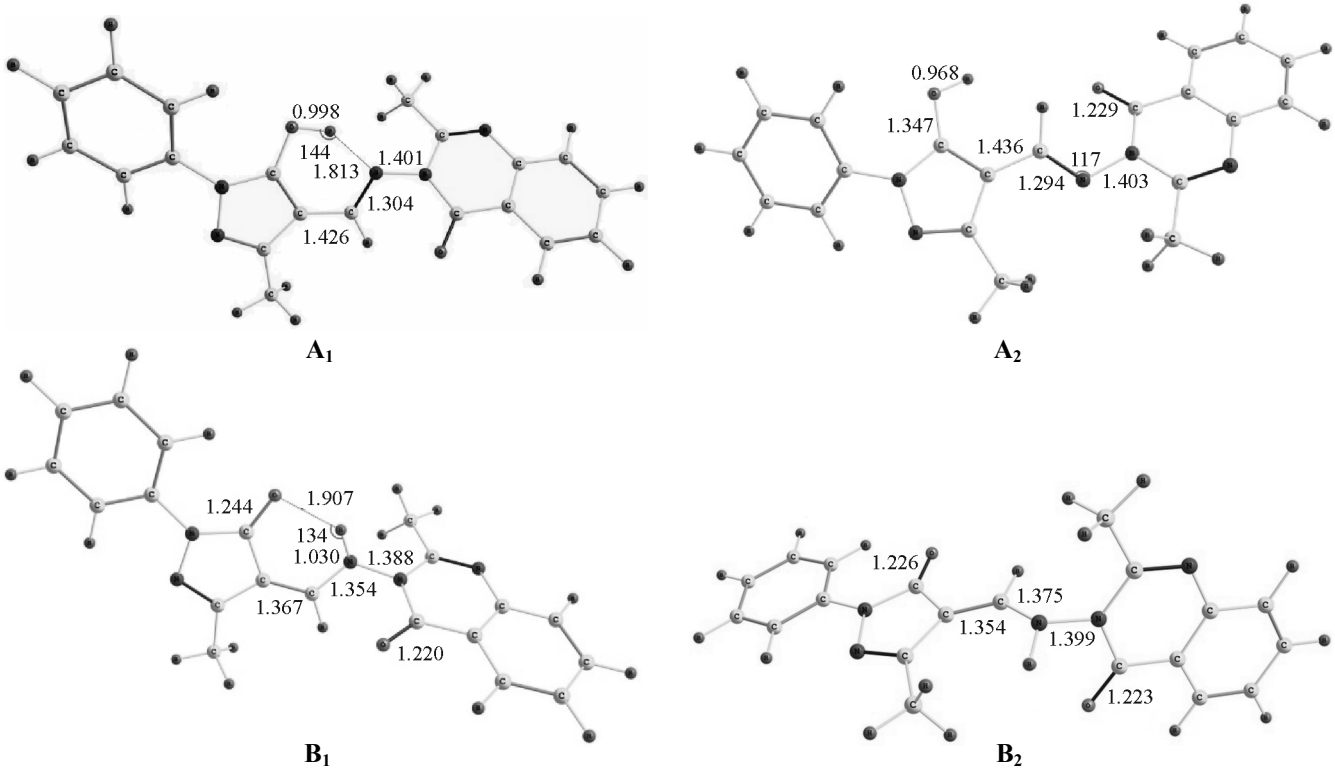


Fig. 1. Principal geometric characteristics (Å, deg.) of conformers **A** and **B**. $\mathbf{A_1}$, $\mathbf{B_1}$ are conformers with intramolecular hydrogen bond, $\mathbf{A_2}$, $\mathbf{B_2}$ are conformers without intramolecular hydrogen bond.

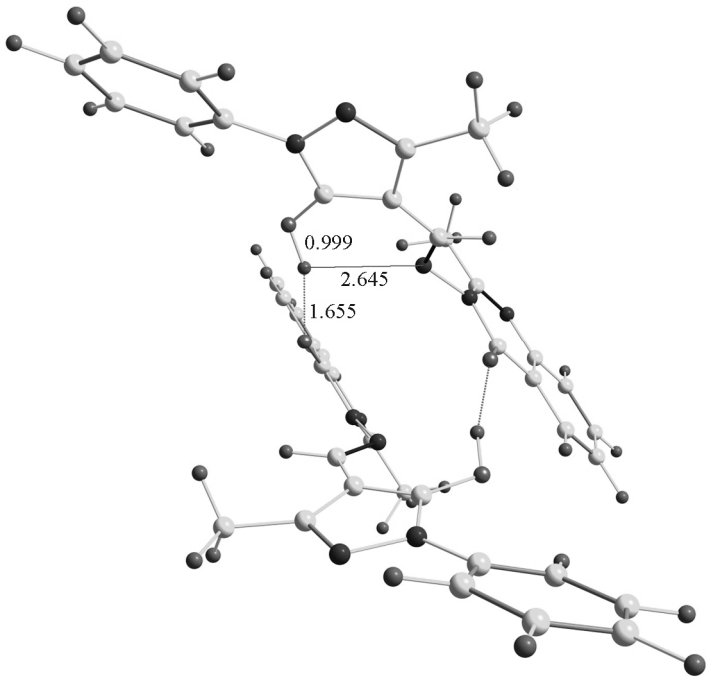


Fig. 2. Structure of dimer **A** (distances in Å, C_2 symmetry).

two signals of methyl groups at 2.2 and 2.5 ppm, signals of aromatic protons in the range 7.1–8.1 ppm, a singlet of azomethine proton CH=N at 8.2 ppm of the corresponding integral intensity, and a very wide signal of one proton in the range 5.0–6.0 ppm. The latter signal disappears upon deuteration, which allows assigning it to an exchangeable proton of OH or NH group.

The shift of the aromatic and methyl protons in the ^{1}H NMR spectrum of compound **III** in $CDCl_3$ is negligible, while the signal of the azomethine proton is shifted upfield by 0.6 ppm and the signal of OH(NH) proton, downfield to 7.3 ppm, which proves its participation in the formation of the hydrogen bond. In the spectrum in acetone-d_6 the signal of OH(NH) proton appears as a broadened singlet at 5.25 ppm, which disappears after addition of D_2O. To determine the location of the exchangeable proton we have taken proton-coupled ^{13}C NMR spectra before and after deuteration. They turned to be identical, which allows assigning the signals at 160 and 164 ppm to the carbonyl carbons and points to the existence of the compound in the NH form. This is also proved by the correlation of this proton with those of one of CH_3 groups in the COSY-spectrum, which is possible only for the NH proton.

Note, that after heating of solution of quinazolinone **III** in aqueous DMSO at 80ºC for 24 h new signals of aromatic and methyl protons appear in the ^{1}H NMR spectrum, apparently, due to the formation of a second tautomer. The ratio of intensities of the methyl protons suggests the ratio of the tautomers of 1 : 4 (new : starting).

In the IR spectrum of compound **III** in mineral oil the intense absorption bands of the C=O, C=C, CH=N groups are observed in the range 1607–1688 cm^{-1}, as well as a very wide intense absorption band in the range 2600–3100 cm^{-1} corresponding to the stretching vibrations of NH or OH group participating in the formation of hydrogen bonds.

To examine the acid–base properties of compound **III** we have registered the electron absorption spectra in water–ethanol solutions at different pH values (Fig. 3).

In neutral and acidic media the spectra practically coincide, at pH = 2 only a small decrease in the intensity of absorption bands at 298 nm and 206 nm is observed, which may be indicative of the presence of quinazolinone in the nonprotonated form even in a strongly acidic medium. In alkaline medium (pH = 12), the longwave band suffers a blue shift by 23 nm, and a shoulder appears at 330 nm, which is due to the formation of the deprotonated form of compound **III**.

The decrease of in the polarity of the solvent causes a hypochromic effect on the longwave absorption band with small shift to short waves (Table 2). Besides, in

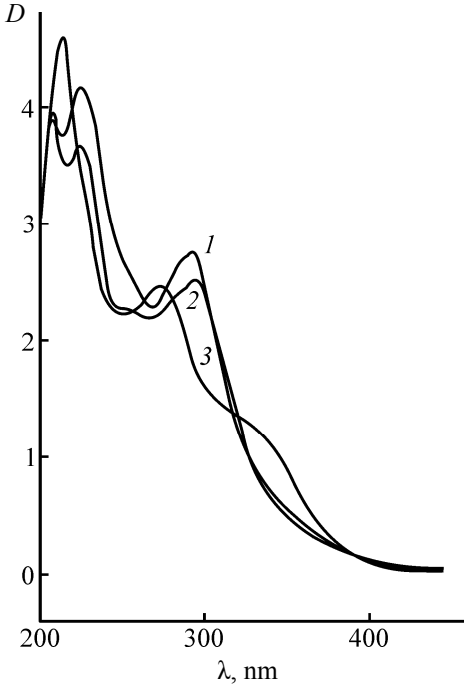


Fig. 3. Electron absorption spectra of 10^{-4} M solution of compound **III** in water–ethanol solution in (*1*) neutral, (*2*) acidic (pH = 2), and (*3*) alkaline medium (pH = 12).

dipolar aprotic solvents, DMSO and acetonitrile, a shoulder is registered on the longwave slope of the absorption band at 315 and 310 nm, respectively, pointing to the partial dissociation of quinazolinone in these solvents. The shoulder is absent in chloroform or toluene solutions.

In electron absorption spectra in ethanol solutions of compound **III** a wide absorption band is observed with a maximum at 294 nm, a shoulder at 277 nm, a notable maximum at 253 nm, and two main maxima at 223 and 206 nm. The assignment of these maxima to specific electron transitions between MOs of quinazolinone was done on the basis of calculations using the nonstationary density functional theory method TD DFT (B3LYP/6-31G**) taking into account the solvent effect by the PCM method. In Fig. 4 the experimental and theoretical spectra are shown, which demonstrate that the difference in the positions of the theoretical and experimental maxima is as small as several nm. In Table 3, the values of parameters of the absorption bands of the theoretical spectrum and their assignment are given.

Electron transition with maximum wavelength is determined by electron transitions from the π-bonding orbital (HOMO) to the π^*-antibonding orbital (LUMO)

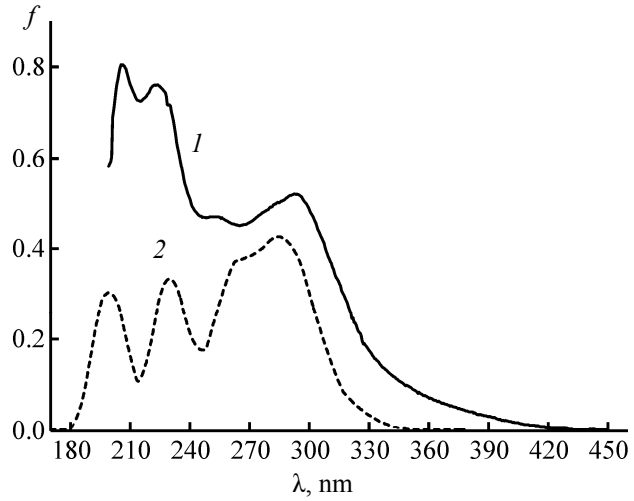


Fig. 4. Electron absorption spectrum of compound **III** in ethanol solution: (*1*) theory and (*2*) experiment.

of the ligand and has a small oscillation strength (*f*). In the experimental spectrum, this electron transition may correspond to the absorption maximum at 365 nm, which can be isolated from the total spectrum by its separation to dispersion components. As seen from Fig. 5, which shows the shape of the HOMO and LUMO of molecule **III**, the HOMO has the maximum contribution from the π MO of the phenylpyrazol part of the molecule, whereas the π^* LUMO is mainly localized on the aminoquinazolinone fragment.

The main longwave maximum at 294 nm is determined by a series of electron transitions, the largest contribution being due to transitions HOMO-1 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO+1. These transitions correspond to electron transfer from the phenylpyrazol to the aminoquinazolinone fragment of the molecule. Other maxima in the spectrum are caused mainly by electron transitions from lower-lying orbitals HOMO-1, HOMO-2 to higher-lying LUMO+2 and LUMO+3.

Table 2. Electron absorption spectra of compound **III**

Solvent	λ_{max}, nm	$\varepsilon \times 10^{-4}$, L mol^{-1} cm^{-1}	log ε
Acetonitrile	286	3.233	4.51
DMSO	290	2.507	4.39
Ethanol	294	2.509	4.4
Chloroform	296	2.95	4.46
Toluene	298	3.474	4.54

Table 3. Calculated wavelengths λ, electron transition energies *E* between the corresponding MOs, contribution of separate electron transitions. and oscillator strengths *f* for molecule **III** (**B$_1$**)

λ_{max}, nm	*E*, eV	Electron transition	Contribution[a], %	*f*
369 (365)[b]	3.3625	HOMO→LUMO	90	0.006
307	4.0407	HOMO-4→LUMO HOMO-2→LUMO HOMO-1→LUMO	28 13 54	0.066
283 (294)	4.3887	HOMO-2→LUMO HOMO-1→LUMO HOMO-1→LUMO+1	42 12 27	0.459
277 (294)	4.4724	HOMO-3→LUMO HOMO-2→LUMO+1 HOMO-1→LUMO+1	20 17 35	0.149
276 (277)	4.4926	HOMO-3→LUMO HOMO-2→LUMO+1	73 12	0.081
271 (277)	4.5817	HOMO-2→LUMO+1 HOMO-1→LUMO+1	55 20	0.283
255 (253)	4.8673	HOMO-2→LUMO+2	71	0.134
252 (253)	4.9210	HOMO→LUMO+3 HOMO→LUMO+4	63 14	0.377
249	4.9885	HOMO-3→LUMO+3 HOMO→LUMO+3 HOMO→LUMO+4	13 16 61	0.176
224 (224)	5.5460	HOMO-5→LUMO+2	55	0.082
222	5.5858	HOMO-8→LUMO HOMO-2→LUMO+3 HOMO-1→LUMO+3	13 19 44	0.097

[a] Contributions of ≥10%. [b] Experimental values.

The studied ligand system is a good complexing agent. By the reaction with Cd(II), Pb(II), Zn(II) acetates metal complexes of 1 : 2 composition (metal : ligand) were isolated. Comparing the IR spectra of complexes of Pb(II) and Cd(II) with quinazolinone **III** showed the disappearance of the absorption band of the NH(OH) group and the shift of the C=O and CH=N absorption bands by 30–40 cm^{-1} to low-frequency region, which confirmed the coordination of these groups to the metal ion. Thus, it can be assumed that these complexes have chelate structure with octahedral surrounding of the central ion.

In the zinc complex, unlike the two above, the C=O group absorption band is shifted by 5–10 cm^{-1} to high frequencies. Since the complex-forming central atoms are isoelectronic, the differently directed shift of the absorption bands is apparently caused by different structure of the complexes. For unambiguous determination of the structure, X-ray diffraction measurements are required.

EXPERIMENTAL

IR spectra were taken on a Varian Scimitar 1000 FT-IR instrument in mineral oil in the range 400–4000 cm^{-1}. Electronic spectra were registered on a Varian Cary 5000 instrument in the range 200–800 nm. Elemental analysis was performed on a Perkin–Elmer 240C instrument in the Laboratory of microanalysis of the Southern Federal University. ^{13}C, ^{1}H, and 2D (COSY) NMR spectra were recorded on a Varian Unity spectrometer (300 MHz) at 200ºC. Mass spectrum was taken on a Shimadzu (GCMS-QP2010SE) spectrometer with direct admission of the sample into the ion source (70 eV, temperature of ionization chamber 2000ºC).

2-Methyl-3-{[(*Z*)-3-methyl-5-oxo-1-phenylpyrazol-4-ylidene)methyl]amino}quinazolin-4-one. To a hot solution of 2 mmol of aldehyde **I** [19] in 15 mL of isopropanol the solution of 2 mmol of amine **II** in 10 mL of isopropanol and 2 drops of acetic acid was

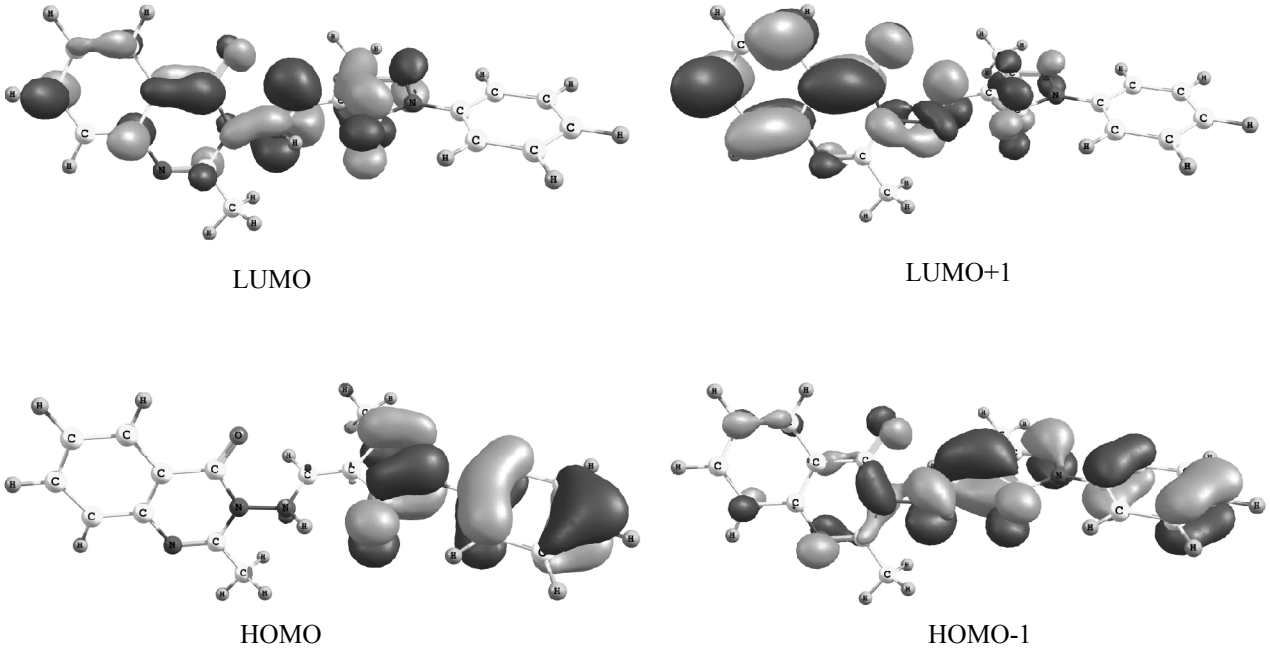


Fig. 5. Shape of frontier MOs of molecule **III**.

added. The obtained solution was refluxed for 5 h and evaporated to half of the volume. The formed precipitate was filtered, washed with ethanol, and crystallized from the mixture ethanol–DMF. Yellow amorphous powder. Yield 68%, mp 223–224ºC. IR spectrum (ν, cm^{-1}): 505, 599, 688, 775, 1200, 1253, 1274, 1502, 1550, 1607, 1638, 1658, 1687, 3077, 3124. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s (3H, CH_3), 2.50 s (3H, CH_3), 5.6 br.s (1H, NH), 7.14 d.d (1H, *J* 7.5, 7.5 Hz), 7.41 d.d (2H, *J* 7.5, 7.5 Hz), 7.56 d.d (1H, *J* 7.5, 7.5 Hz), 7.68 d (1H, *J* 7.5), 7.88 d.d.d (1H, *J* 7.5, 7.5, 1.5 Hz), 7.97 d (2H, *J* 7.5 Hz), 8.14 d.d.d (1H, *J* 7.5, 7.5, 0.9 Hz), 8.20 s (1H, =CH–N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (3H, CH_3), 2.63 s (3H, CH_3), 7.11 d.d (1H, *J* 7.5, 7.5 Hz), 7.33 br d.d (3H, $2CH_{arom}$ + NH, *J* 7.5, 7.5 Hz), 7.49 d.d.d (1H, *J* 7.5, 7.5, 0.9 Hz), 7.50 s (1H, =CH–N), 7.63 d (1H, *J* 7.5), 7.49 d.d.d (1H, *J* 7.5, 7.5, 1.5 Hz), 7.86 d (2H, *J* 7.5 Hz), 8.21 d.d (1H, *J* 7.5, 1.2 Hz). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.24 s (3H, CH_3), 2.66 s (3H, CH_3), 5.25 br.s (1H, NH), 7.14 d.d.d (1H, *J* 7.5, 7.5, 1.2 Hz), 7.40 d.d.d (2H, *J* 7.5, 7.5, 2.0 Hz), 7.56 d.d.d (1H, *J* 7.5, 7.5, 1.2 Hz), 7.66 d.d (1H, *J* 7.5, 0.9 Hz), 7.87 d.d.d (1H, *J* 7.5, 7.5, 1.5 Hz), 8.08 d.d (2H, *J* 7.5, 1.2 Hz), 8.16 s (1H, =CH–N), 8.19 d.d (1H, *J* 7.5, 1.2 Hz). Mass spectrum, *m/z* (I_{rel}): 359 (24.9) $[M]^+$, 201 (4.0), 199 (16.9), 186 (9.2), 170 (7.6), 160 (100), 144 (6.4), 135 (13.8), 127 (8.2), 125 (23.6), 118 (15.0), 104 (8.5), 91 (31.9), 77 (48.9), 67 (15.6), 63 (11.6), 51 (14.1). Found, %: C 67.31; H 4.15; N 19.94. $C_{20}H_{17}O_2N_5$. Calculated, %: C 66.84; H 4.77; N 19.49.

Synthesis of metal complexes IV *(general procedure).* To the suspension of 1 mmol of ligand **III** in 5 mL of methanol hot solution of 0.5 mmol of the corresponding metal acetate in 5 mL of methanol was added and refluxed for 4 h, then to the obtained solution 0.01 mol of triethylamine was added and refluxed for 1 h. The precipitate formed upon cooling was filtered, twice washed with hot methanol, and dried in a vacuum.

Complex of Cd(II). Yield 35%, white amorphous powder, mp 245ºC. IR spectrum, ν, cm^{-1}: 511, 609, 697, 768, 943, 1059, 1177, 1240, 1320, 1536, 1594, 1612, 1658. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.10 s (3H, CH_3), 2.57 s (3H, CH_3), 7.07 d,d (1H, *J* 6.6, 6.6 Hz), 7.23 d.d (2H, *J* 7.5, 7.5 Hz), 7.45 d.d (1H, *J* 7.5, 7.5 Hz), 7.59 d (1H, *J* 8.5 Hz), 7.76 m (3H), 8.07 d (1H, *J* 8.5 Hz), 8.29 t (1H, =CH–N, *J* 15.5 Hz). Found, %: C 57.59; H 3.37; N 17.21; Cd 13.83. $C_{40}H_{32}O_4N_{10}Cd$. Calculated, %: C 57.94; H 3.89; N 16.89; Cd 13.56.

Complex of Zn(II). Yield 80%, white crystals, mp 233ºC. IR spectrum, ν, cm^{-1}: 490, 514, 607, 691, 758, 1186, 1245, 1322, 1554, 1597, 1618, 1678, 1691. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.11 s (3H, CH_3), 2.54 s (3H, CH_3), 6.38 m (3H), 7.26 d.d (2H, *J* 7.5, 1.5 Hz), 7.39 d (1H, *J* 7.5 Hz), 7.45 d.d (1H, *J* 7.5,

7.5 Hz), 7.67 d.d.d (1H, *J* 7.5, 7.5, 1.2 Hz), 8.10 d (1H, *J* 7.5 Hz), 8.48 s (1H, =CH–N). Found, %: C 62.34; H 4.41; N 17.76; Zn 7.84. $C_{40}H_{32}O_4N_{10}Zn$. Calculated, %: C 61.96; H 4.16; N 18.06; Zn 7.57.

Complex of Pb(II). Yield 32%, white crystals, mp 252ºC. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, CH_3), 2.60 s (3H, CH_3), 7.00 d.d (1H, *J* 7.2, 7.2 Hz), 7.27 m (3H), 7.45 d.d (1H, *J* 7.5, 7.5 Hz), 7.60 d (1H, *J* 8.5 Hz), 7.77 d.d (1H, *J* 7.2, 7.2 Hz), 7.98 m (2H, CH_{arom}+ =CH–N), 8.07 d (1H, *J* 7.2 Hz).

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