New octahedral Zn^{II} and Cd^{II} complexes based on azo derivatives and azomethines of pyrazole-5-thione

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New metal chelates of Zn^{II} and Cd^{II} (ML_2) based on (4*Z*)-3-methyl-1-phenyl-5-thioxo-1,5-dihydro-4*H*-pyrazol-4-one quinolin-8-ylhydrazone (HL^1) and (4*Z*)-5-methyl-2-phenyl-4-[(quinolin-8-ylimino)methyl]-2,4-dihydro-3*H*-pyrazole-3-thione (HL^2) were synthesized. The structures of the metal chelates were studied by EXAFS and NMR (^1H, ^{13}C, and ^{111}Cd) spectroscopy. The structure of the $Cd(L^1)_2$ complex was established by X-ray diffraction analysis. The complexes have pseudooctahedral structures with the N_4S_2 ligand environment.

Key words: azomethines, azo compounds, metal chelates of zinc(II) and cadmium(II), X-ray diffraction analysis, EXAFS and NMR spectroscopy.

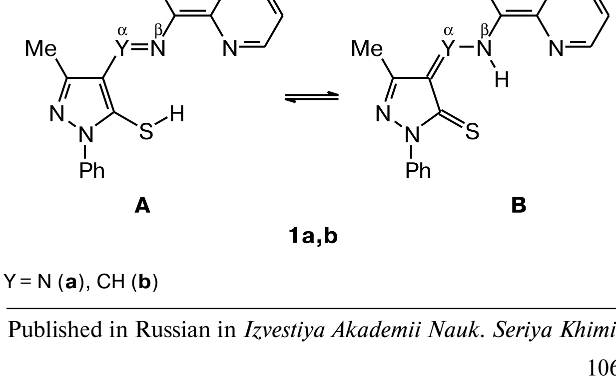
Investigations of *o*-hydroxy(mercapto)azomethines and azo compounds of aromatic and heteroaromatic series are of considerable interest in connection with the problems of tautomerism and complexation of chelating ligand systems.[1—21]

In the present study, we synthesized and characterized zinc(II) and cadmium(II) metal chelates based on the azo derivative of pyrazole-5-thione (**1a**) and enamine (**1b**) containing the coordinatively active quinoline substituent.

Ligands **1a,b** were synthesized according to procedures described in our earlier publications.[5,8,22]

The tautomeric equilibrium **A** $\rightleftharpoons$ **B** is typical of azo compounds and azomethines (Scheme 1).[1,3,4] Earlier,[5,8,22] we have demonstrated (by X-ray diffraction analysis and ^1H NMR spectroscopy) that compound **1a** in solution exists in the thioxohydrazone form **A**, whereas **1b** has the enamine structure **B**.

Scheme 1

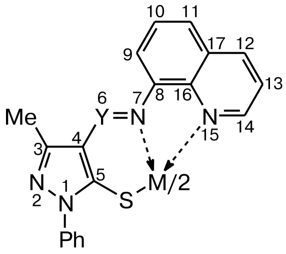


1a,b

Y = N (**a**), CH (**b**)

Complexes **2** and **3**, like the chelates described earlier,[8] were synthesized by the direct reaction of 2 equiv. of ligands **1a,b** (LH) with 1 equiv. of the corresponding metal acetates in methanol and have the composition ML_2.

The structures of chelate compounds **2** and **3** were established by X-ray diffraction analysis, EXAFS spectroscopy, and heteronuclear ^1H, ^{13}C, and ^{111}Cd NMR spectroscopy.



2a,b, **3a,b**

M = Cd (**2**), Zn (**3**); Y = N (**a**), CH (**b**)

X-ray diffraction study demonstrated (Fig. 1) that the Cd atom in complex **2a** is in a pseudooctahedral N_4S_2 environment with the *cis* arrangement of the sulfur atoms (S(1)—Cd(1)—S(1´), 103.08(4)°). The ligands coordinated to the Cd atom are orthogonal to each other; the dihedral angle is 95.7°. The five-membered metallocycles adopt an envelope conformation. The Cd(1)N(4)C(11)C(19)N(5) ring has an ideal envelope conformation with the Cd(1) atom deviating from the N(4)C(11)C(19)N(5) plane by 0.298 Å and a folding angle of 8.9°. The Cd(1)N(4´)C(11´)C(19´)C(5´)

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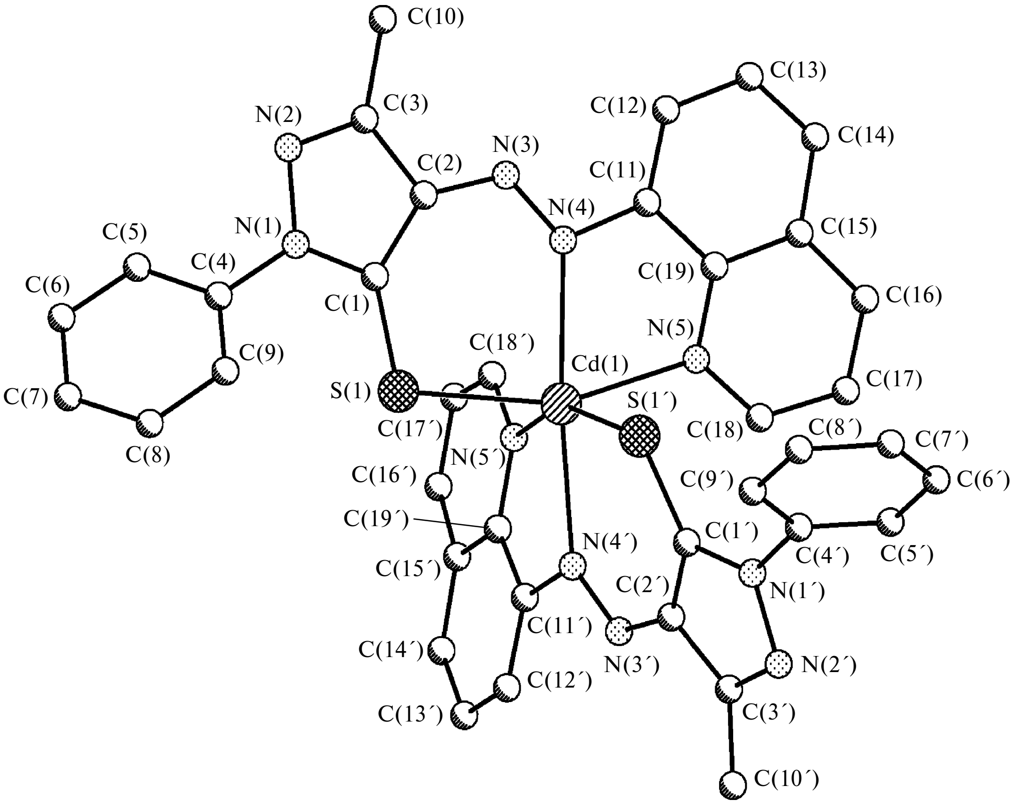

Fig. 1. Overall view of metal chelate **2a**.

metallocycle has a distorted envelope conformation with the Cd(1) atom deviating from the plane of the other atoms by 0.5257 Å and a folding angle of 15.5°. The Cd(1)S(1)C(1)C(2)N(3)N(4) and Cd(1)S(1´)C(1´)C(2´)N(3´)N(4´) six-membered metallocycles adopt a sofa conformation with the metal and sulfur atoms deviating in opposite directions from the plane by 0.081 and –0.1092 Å (0.29 and –0.23 Å), respectively. The presence of two five-membered metallocycles, which are sterically more hindered than the six-membered rings, is responsible for deviations from the octahedral symmetry of the coordination polyhedron; the corresponding bond angles deviate from 90° within 19.3°. In metal chelate **2a**, the Cd atom is coordinated to the N$_\beta$ atoms of the azo groups of both ligands (Cd(1)—N(4´) and Cd(1)—N(4) are 2.386(3) and 2.395(3) Å, respectively) to form two six-membered metallocycles. This coordination has been observed in a series of azo complexes.[3,8—14] An alternative coordination of the N=N group of azo compounds resulting in two five-membered rings or a five-membered ring and a six-membered ring was also described and established by X-ray diffraction.[2—4,15—21] The Cd(1)—S(1) bond length differs from the Cd(1)—S(1´) bond length by ~0.04 Å and these bonds lengths are in the range of distances observed in octahedral Cd^{II} complexes with the N$_4$S$_2$-ligand environment.[23—27] The Cd—N^{quin} distances (2.345(3) and 2.405(3) Å) are close to the corresponding distances observed[26] for the pyridine ligands (2.472 and 2.424 Å) in the pseudooctahedral complex bis(2-pyridineformamido-3-piperidylthiosemicarbazonato)cadmium(II). The bond lengths and bond angles in the two ligands of one molecule of the complex are virtually identical. A slight variation in the conformation, in particular, in the twist angles of the phenyl group with respect to the pyrazole ring (39.8 and 54.2°) and of the quinoline group with respect to the N=N double bond (N(3)N(4)C(11)C(12) and N(3´)N(4´)C(11´)C(12´) torsion angles are 4.7 and 20.1°, respectively), is attributable to the crystal packing effects. The analysis of intermolecular contacts demonstrated that only one of the ligands in the crystal is involved in stacking interaction (shortest C...C distances are 3.32—3.36 Å) between the pyrazole and quinoline rings of the adjacent molecules, thus linking the molecules to form centrosymmetric dimers.

The structural data for the nearest environment of the zinc atom in complex **3b** were obtained by EXAFS spectroscopy. Since the presence of an additional N-donor fragment of the quinoline ring complicates the interpretation of the EXAFS spectra, we synthesized the tetracoordinated model compound bis{3-methyl-1-phenyl-4-[(*E*)-(phenylimino)methyl]-1*H*-pyrazole-5-thiolato}Zn(II) (**4**), which has been described earlier.[28,29]

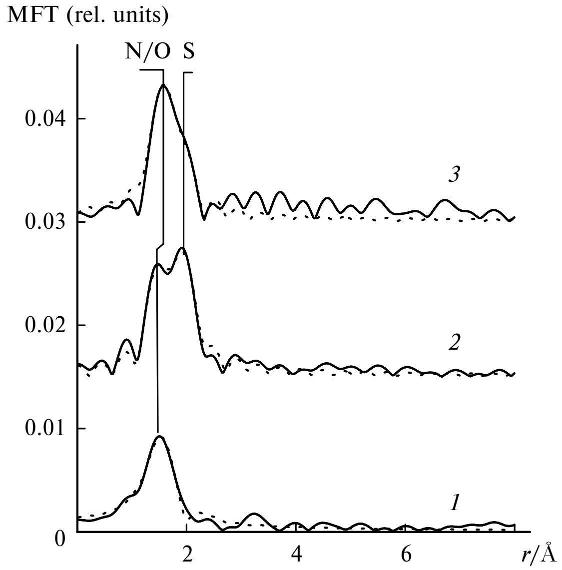

Fig. 2. EXAFS data for zinc acetate (*1*), complex **4** (*2*), and chelate **3b** (*3*) analyzed using the multiresolution Fourier transform (MFT).

The EXAFS data for complexes **3b** and **4** and zinc acetate were analyzed with the use of the multiresolution Fourier transforms (MFT) and are shown in Fig. 2. The parameters of the nearest environment of the zinc atom in these compounds, which were determined by fitting the calculated values $\chi(k)$ for the models to the experimental EXAFS spectra, are given in Table 1.

For the standard compound, *viz*., zinc acetate, MFT has one unsplit main peak. This peak corresponds to scattering of the photoelectron wave at the first coordination sphere consisting of four oxygen atoms. Unlike MFT for zinc acetate, MFTs for complexes **3b** and **4** (see Fig. 2) clearly show splitting of the first main peak due to the presence of two different Zn—N and Zn—S distances in the first coordination sphere. It can also be noted that the peak corresponding to scattering at the nitrogen atoms in the MFT for complex **3b** has a larger amplitude compared to the analogous peak in MFT of complex **4**. We constructed models of the nearest atomic environment of the zinc atoms in these complexes, where the first coordination sphere of the zinc atom in molecule **4** consists of two nitrogen atoms and two sulfur atoms $[ZnN_2S_2]$, whereas the first coordination sphere in molecule **3b** contains additionally two nitrogen atoms (N^{quin}) of the quinoline fragment $[ZnN_2N^{quin}{}_2S_2]$. The fitting of the calculated EXAFS spectra of these models to the experimental spectra of the samples under study gave Q similar to those obtained for the standard compounds, which confirms the reliability of the models. The structural parameters for the atoms of the first coordination spheres in these compounds are given in Table 1. The Zn—S distances in both complexes are only slightly different, whereas the Zn—N distances in these complexes have different values. The fact that the Zn—N distances in complex **3b** are longer than those in complex **4** is associated with the contribution of the longer additional Zn—N^{quin} bonds to the radius of the first coordination sphere of **3b**. The first coordination sphere of complex **3b** consists of the N^{quin} and N atoms, and its radius was averaged over all the Zn—N^{quin} and Zn—N distances.

Table 1. Structural data obtained from analysis of the EXAFS spectra of the complexes

Compound	n	R/Å	σ^2/Å^2	Atom	Q (%)
$Zn(OAc)_2$	4	2.03	0.0082	O	7.1
4	2	1.98	0.0020	N	4.6
	2	2.34	0.0018	S	—
3b	4	2.04	0.0021	N/N′	6.5
	2	2.37	0.0029	S	—

Note. R is the radius of the coordination spheres, n is the coordination number, σ^2 is the Debye—Waller factor. The Q factor characterizes the fitting quality.

Therefore, the X-ray diffraction study and EXAFS spectroscopy demonstrated that complexes **2a** and **3b** are isostructural. It should be noted that the Zn—N^{quin} and Zn—S distances in complex **3b** determined by EXAFS spectroscopy are shorter than those in bis(2-pyridineformamido-3-piperidylthiosemicarbazonato)zinc(II).[26]

The octahedral structures of complexes **2** and **3** in solution were confirmed by heteronuclear ^1H, ^{13}C, and ^{111}Cd NMR spectroscopy[30—32] (Tables 2—7).

In the ^1H NMR spectra of complex **2a**, the signals for the H(9), H(10), and H(11) atoms and the Me group are shifted downfield, whereas the signals for the H(12), H(13), and H(14) protons of the Ph fragment are shifted upfield relative to the chemical shifts of ligand **1a** (see Tables 2 and 4).

The most substantial changes in the chemical shifts are observed for the signals of the H(13) and H(14) protons of the quinoline ring and the *o*-protons of the Ph fragment. The same tendency persists for metal chelates **2b** and **3a,b**, except for the signals of the H(12) protons of complex **2b**, which are shifted downfield by 0.05 ppm. In the spectra of complexes **2b** and **3b**, the signals for the H(6) protons of the CH=N bond are also shifted downfield (see Tables 5 and 7).

A comparison of the constants $J_{H,H}$ for complex **2a** and ligand **1a** demonstrated that complexation causes changes in the Ph fragment ($J_{H,H}$ are averaged, $^3J_{H_o,H_m} = {}^3J_{H_m,H_p} = 7.7$ Hz), whereas these constants for the quinoline moiety of the molecule remain unchanged upon complexation (see Table 4). In the spectrum of complex **3a**, the coupling constants for the protons of the quinoline fragment also remain unchanged, and the constants for the phenyl substituent vary only slightly (±0.2 Hz). Substantially larger changes in the coupling constants for the

Table 2. ^{1}H NMR spectra of ligand **1a** and chelate complexes **2a** and **3a** (in $CDCl_3$)

Atom, group	δ			$J_{H,H}$/Hz						T_1*/s		
	1a	**2a**	**3a**	**1a**		**2a**		**3a**		**1a**	**2a**	**3a**
				^3J	^4J	^3J	^4J	^3J	^4J			
H(9)	8.25	8.29	8.41	7.6	—	7.6	1.6	7.6	1.4	2.11	1.41	1.52
H(10)	7.63	7.68	7.73	7.6; 8.2	—	7.6; 8.2	—	7.6; 8.2	—	1.69	0.95	1.05
H(11)	7.72	7.75	7.74	8.2	—	8.2	1.6	8.2	1.4	2.03	1.01	1.04
H(12)	8.19	8.17	8.14	8.4	1.6	8.4	1.7	8.4	1.7	2.17	1.06	1.15
H(13)	7.49	7.27	7.25	8.4; 4.2	—	8.4; 4.4	—	8.4; 4.5	—	2.02	1.01	1.08
H(14)	9.01	8.43	8.26	4.2	1.6	4.4; 12.9**	1.7	4.5	1.7	2.31	1.57	1.68
o-H_{Ph}	8.02	7.65	7.65	8.1	—	7.7	—	8.3	—	2.75	1.68	1.85
m-H_{Ph}	7.50	7.34	7.32	8.1; 7.5	—	7.7; 7.7	—	8.3; 7.3	—	2.32	1.28	1.45
p-H_{Ph}	7.35	7.23	7.23	7.5	—	7.7	—	7.3	—	2.97	1.08	1.60
Me	2.42	2.59	2.60	—	—	—	—	—	—	1.40	0.78	0.80
NH	17.33	—	—	—	—	—	—	—	—	2.44	—	—

* Spin-lattice relaxation times.

** $J_{^{111}Cd,^1H}$.

Table 3. ^{13}C NMR spectra of ligand **1a** and chelate complexes **2a** and **3a** (in $CDCl_3$)

Atom, группа	δ			$^1J_{C,H}$/Hz			T_1/s		
	1a	**2a**	**3a**	**1a**	**2a**	**3a**	**1a**	**2a**	**3a**
C(3)	151.48	153.75	154.95	—	—	—	13.36	6.04	6.49
C(4)	135.27	136.01	136.14	—	23.2*	—	18.74	9.76	14.20
C(5)	165.85	146.67	149.85	—	12.2*	—	11.92	6.99	10.37
C(8)	138.79	146.32	146.38	—	21.4*	—	15.92	4.86	7.79
C(9)	114.35	116.74	116.45	164.3	164.0, 3.0*	164.9	1.11	0.32	0.43
C(10)	127.00	128.02	128.32	162.5	162.7	161.2	1.21	0.38	0.49
C(11)	125.28	127.10	126.19	163.1	163.7	162.5	0.86	0.41	0.45
C(12)	135.81	138.17	137.39	162.8	162.9	163.4	0.83	0.31	0.33
C(13)	122.20	121.93	122.14	164.6	167.0, 7.9*	166.7	1.14	0.34	0.38
C(14)	150.06	148.64	146.46	180.4	180.6, 4.3*	180.3	1.31	0.35	0.39
i-C_{Ph}	137.14	139.17	139.20	—	—	—	10.85	6.07	9.42
o-C_{Ph}	123.61	125.92	125.32	162.1	161.9	162.8	2.72	0.96	1.30
m-C_{Ph}	128.63	128.32	128.37	161.8	160.6	160.6	2.77	0.98	1.25
p-C_{Ph}	127.31	127.49	127.29	162.2	161.3	163.1	1.02	0.35	0.45
C(16)	138.64	139.96	138.84	—	7.9*	—	12.67	5.19	7.63
C(17)	128.41	128.85	129.05	—	5.1*	—	9.29	3.17	3.95
Me	11.04	11.65	11.63	129.5	128.6	128.7	3.94	1.93	2.26

* $J_{^{111}Cd,^{13}C}$/Hz.

protons of both the quinoline and phenyl fragments are observed for azomethine complexes **2b** and **3b** (see Table 7).

Measurements of ^{1}H spin-lattice relaxation times demonstrated that T_1 for complexes **2a** and **3a** sharply decrease compared to T_1 for compound **1a** (see Table 4), whereas these changes are less significant for complexes **2b** and **3b** (see Table 7).

In the ^{111}Cd NMR spectrum of compound **2a**, the signal is observed at δ –415.80, which corresponds to analogous cadmium complexes.[30]

Investigation of compound **2a** by ^{13}C NMR spectroscopy (see Tables 3 and 4) provided the most detailed information on the structure of this complex. The signals for the C(3) and C(4) atoms of the pyrazole fragment and the signals for the C(8), C(9), C(10), C(11), C(12), C(16), and C(17) atoms of the quinoline moiety of the molecule are shifted downfield, whereas the signals for the C(5), C(13), and C(14) atoms are shifted upfield. The large change in the chemical shift of ^{13}C(5) ($\Delta\delta = -19.18$) can be attributable to the fact that the hydrazone structure of the ligand **B** is rearranged into the azo form **A** upon com-

Table 4. ^{1}H and ^{13}C NMR spectra of chelate complexes **2a** and **3a** relative to compound **1a** (in CDCl$_3$)

Atom, group	^{1}H NMR				^{13}C NMR					
	$\Delta\delta$		ΔT_1/s		$\Delta\delta$		$\Delta^1J_{C,H}$/Hz		ΔT_1/s	
	2a	**3a**	**2a**	**3a**	**2a**	**3a**	**2a**	**3a**	**2a**	**3a**
C(3)	—	—	—	—	+2.27	+2.47	—	—	−7.32	−6.87
C(4)	—	—	—	—	+0.74	+0.87	—	—	−8.98	−4.54
C(5)	—	—	—	—	−19.18	−16.00	—	—	−4.93	−1.55
C(8)	—	—	—	—	+7.53	+7.59	—	—	−11.06	−8.13
C(9)H	+0.04	+0.16	−0.70	−0.59	+2.39	+2.10	−0.3	+0.6	−0.79	−0.68
C(10)H	+0.05	+0.10	−0.74	−0.64	+1.02	+1.32	+0.5	−1.3	−0.83	−0.72
C(11)H	+0.03	+0.02	−1.02	−0.99	+1.82	+0.91	+0.6	−0.6	−0.45	−0.41
C(12)H	−0.02	−0.05	−1.11	−1.02	+2.36	+1.58	+0.1	+0.6	−0.52	−0.50
C(13)H	−0.22	−0.24	−1.01	−0.94	−0.27	−0.06	+2.4	+2.1	−0.80	−0.76
C(14)H	−0.58	−0.75	−0.74	−0.63	−1.42	−3.60	+0.2	−0.1	−0.96	−0.92
i-C$_{Ph}$	—	—	—	—	+2.03	+2.06	—	—	−4.78	−1.43
o-CH$_{Ph}$	−0.37	−0.37	−1.07	−0.90	+2.31	+1.71	−0.2	+0.7	−1.76	−1.42
m-CH$_{Ph}$	−0.16	−0.18	−1.04	−0.87	−0.31	−0.26	−1.2	−1.2	−1.79	−1.52
p-CH$_{Ph}$	−0.12	−0.12	−1.89	−1.37	+0.18	−0.02	−0.9	+0.9	−0.67	−0.57
C(16)	—	—	—	—	+1.32	+0.20	—	—	−7.48	−5.04
C(17)	—	—	—	—	+0.44	+0.64	—	—	−6.12	−5.34
Me	+0.17	+0.18	−0.62	−0.60	+0.61	+0.59	−0.9	−0.8	−2.01	−1.68

Table 5. ^{1}H NMR spectra of azomethine **1b** and chelate complexes **2b** and **3b** (in CDCl$_3$)

Atom, group	δ			$J_{H,H}$/Hz						T_1/s		
	1b	**2b**	**3b**	**1b**		**2b**		**3b**		**1b**	**2b**	**3b**
				^3J	^4J	^3J	^4J	^3J	^4J			
H(6)	8.43	8.78	8.84	13.8	—	17.0*	—	—	—	0.88	0.79	0.81
H(9)	7.63	7.64	7.75	7.6	1.1	—	—	7.3	1.1	0.82	0.90	0.76
H(10)	7.36	7.62	7.65	7.6; 7.7	—	—	—	7.3; 8.1	—	1.30	0.90	0.98
H(11)	7.48	7.63	7.59	7.7	1.1	—	—	8.1	1.1	1.57	0.90	1.08
H(12)	8.04	8.09	8.02	8.4	1.6	8.6	1.6	8.3	1.6	1.54	1.16	1.16
H(13)	7.40	7.20	7.13	8.4; 4.2	—	8.6; 4.4	—	8.3; 4.4	—	1.34	1.08	1.07
H(14)	8.89	8.43	8.41	4.2	1.6	4.4; 11.4*	1.6	4.4	1.6	1.82	1.64	1.63
o-H$_{Ph}$	8.07	7.58	7.53	8.6	1.2	8.6	1.2	7.7	1.4	2.02	1.72	1.73
m-H$_{Ph}$	7.47	7.33	7.29	8.6; 7.4	—	8.6; 7.5	—	7.7; 7.4	—	0.62	1.34	1.37
p-H$_{Ph}$	7.32	7.23	7.18	7.4	1.2	7.5	1.2	7.4	1.4	2.10	1.60	1.73
Me	2.26	2.47	2.51	—	—	—	—	—	—	0.88	0.69	0.71
NH	15.13	—	—	13.8	—	—	—	—	—	1.25	—	—

$J_{^{111}Cd,^{1}H}$.

plexation (see Tables 3 and 4). In the ^{13}C NMR spectrum of chelate **3a**, the changes in the positions of the signals relative to those of ligand **1b** are analogous to those observed in the spectra of the corresponding azomethine complexes **2b** and **3b**, except for the peak of C(11) of compounds **2b** and **3b**, which is shifted upfield (see Tables 3, 4, 6, and 7). The rearrangement of the enamine form of the free ligand to the azomethine form upon complexation is also accompanied by a substantial change in the chemical shift of C(5) ($\Delta\delta$ = −15.18 (**2b**) and −11.96 (**3b**)) (see Tables 6 and 7).

Measurements of the spin-spin coupling constants demonstrated that the constant $^1J_{C,H}$ changes only slightly upon the involvement of ligand **1a** in complex **2a** (see Tables 3 and 4), whereas the constants $J_{Cd,C}$ give essential information on the structure of the cadmium complex. The vicinal constant $^3J_{Cd,C(4)}$ = 23.2 Hz in complex **2a** can be manifested along both the Cd—N(7)—N(6)—C(4) and Cd—S—C(5)—C(4) chains. The geminal constant $^2J_{Cd,C(5)}$ = 12.2 Hz is much smaller. The spin-spin coupling between ^{111}Cd and ^{13}C$_8$ also belongs to vicinal couplings ($^3J_{Cd,C(8)}$ = 21.4 Hz) and occurs along the

Table 6. ^{13}C NMR spectra of azomethine **1b** and chelate complexes **2b** and **3b** (in $CDCl_3$)

Atom, группа	δ			$^1J_{C,H}$/Hz			T_1/s	
	1b	**2b**	**3b**	**1b**	**2b**	**3b**	**1b**	**3b**
C(3)	151.60	152.57	152.59	—	2.0*	—	7.72	5.73
C(4)	114.86	115.76	116.04	—	16.4*	—	12.04	6.03
C(5)	170.51	155.33	158.55	—	11.7*	—	8.06	11.51
C(6)	144.66	158.79	157.67	168.5	155.1, 4.5*	155.4	0.65	0.48
C(8)	139.23	139.95	139.68	—	11.6*	—	8.75	6.40
C(9)	114.18	116.72	115.52	161.0	159.8, 6.6*	159.1	0.68	0.43
C(10)	126.20	127.97	128.00	164.2	162.5	162.4	0.70	0.48
C(11)	125.05	124.45	124.08	163.6	163.4	169.3	0.52	0.36
C(12)	135.65	137.63	137.70	162.8	163.1	163.4	0.52	0.44
C(13)	122.31	122.09	122.15	164.6	166.3, 6.5*	166.1	0.66	0.42
C(14)	149.94	148.22	146.57	180.5	180.8, 3.8*	—	0.71	0.49
i-C_{Ph}	135.09	139.65	139.40	—	—	—	8.87	6.55
o-C_{Ph}	124.06	126.07	125.64	163.8	165.1	165.0	1.45	0.98
m-C_{Ph}	128.31	128.28	128.03	160.7	163.8	163.5	1.44	1.04
p-C_{Ph}	126.82	127.26	127.02	161.5	161.2	161.0	0.59	0.39
C(16)	135.15	146.42	145.83	—	11.7*	—	6.31	4.69
C(17)	128.43	128.67	128.73	—	6.0*	—	5.77	5.28
Me	11.49	11.93	11.91	128.4	127.8	127.3	2.51	1.50

* $J_{^{111}Cd,^{13}C}$/Hz.

Table 7. ^1H and ^{13}C NMR spectra of chelate complexes **2b** and **3b** relative to compound **1b** (in $CDCl_3$)

Atom, group	^1H NMR				^{13}C NMR				
	Δδ		ΔT_1/s		Δδ		$\Delta^1J_{C,H}$/Hz		ΔT_1/s
	2b	**3b**	**2b**	**3b**	**2b**	**3b**	**2b**	**3b**	**3b**
C(3)	—	—	—	—	+0.97	+0.99	—	—	−1.99
C(4)	—	—	—	—	+0.90	+1.18	—	—	−5.99
C(5)	—	—	—	—	−15.18	−11.96	—	—	+3.45
C(6)H	+0.35	+0.41	−0.09	−0.07	+14.13	+13.01	−13.4	−13.1	−0.17
C(8)	—	—	—	—	+0.72	+0.45	—	—	−2.35
C(9)H	+0.01	+0.09	+0.08	−0.06	+2.54	+1.34	−1.2	−1.9	−0.25
C(10)H	+0.26	+0.29	−0.40	−0.32	+1.77	+1.80	−1.7	−1.8	−0.22
C(11)H	+0.15	+0.11	−0.67	−0.49	−0.60	−0.97	−0.2	+5.7	−0.16
C(12)H	+0.05	−0.02	−0.38	−0.38	+1.98	+2.05	+0.3	+0.6	−0.08
C(13)H	−0.20	−0.27	−0.26	−0.27	−0.22	−0.16	+1.7	+1.5	−0.24
C(14)H	−0.46	−0.48	−0.18	−0.19	−1.72	−3.37	+0.3	—	−0.22
i-C_{Ph}	—	—	—	—	+4.56	+4.31	—	—	−2.32
o-CH_{Ph}	−0.49	−0.54	−0.30	−0.29	+2.01	+1.58	+1.3	+1.2	−0.47
m-CH_{Ph}	−0.14	−0.18	−0.28	−0.25	−0.03	−0.28	+3.1	+2.8	−0.40
p-CH_{Ph}	−0.09	−0.14	−0.50	−0.27	+0.44	+0.20	−0.3	−0.5	−0.20
C(16)	—	—	—	—	+11.27	+10.68	—	—	−1.62
C(17)	—	—	—	—	+0.24	+0.30	—	—	−0.49
Me	+0.21	+0.25	−0.19	−0.17	+0.44	+0.42	−0.6	−1.1	−1.01

Cd—N(15)—C(16)—C(8) chain. An analogous tendency for changes in the coupling constants is observed in the spectrum of complex **2b**, although these changes are somewhat smaller in magnitude (see Tables 6 and 7). The geminal constants $^2J_{Cd,C(5)}$ = 11.7 and $^2J_{Cd,C(6)}$ = 4.5 Hz are much smaller than those in compound **2a**. The occurrence of the spin-spin coupling constants between cadmium and the C(9), C(13), C(14), C(16), and C(17) atoms is direct evidence that metal is bound to the nitrogen atoms of the Y=N groups and the quinoline ring (see Tables 3 and 6).

The NMR spectroscopic data on the changes in the spin-spin coupling constants and the chemical shifts indicate that the azomethine and azo complexes of zinc and cadmium are isostructural.

To summarize, the results of X-ray diffraction study, EXAFS spectroscopy, and heteronuclear NMR spectroscopy allow one to unambiguously reveal additional coordination of the N atom of the quinoline fragment of the azomethine and azo ligands resulting in the formation of octahedral zinc and cadmium chelates.

Experimental

The ^{1}H ^{13}C, and ^{111}Cd NMR spectra were recorded on a Varian UNITY-300 spectrometer (300 MHz) using internal field stabilization at the D resonance line in $CDCl_3$.

The zinc K-edge EXAFS spectrum was measured on a laboratory EXAFS spectrometer designed on the basis of a DRON-3 diffractometer. X-ray radiation was split into a spectrum using a (1340) quartz crystal monochromator. The extended X-ray absorption fine structure (EXAFS) $\chi(k)$ was resolved according to a standard procedure.[33] The Fourier transformation of the EXAFS spectrum was performed in the range of photoelectron wave vectors $k = 3.5—13.0$ A^{-1} with the weighting function $k = 2$. The scattering phases and amplitudes of the photoelectron wave required for the construction of the model spectrum were calculated with the use of the FEFF5 program.[34]

X-ray diffraction study of complex 2a. Crystals are triclinic, at 110 K, $a = 11.9283(8)$ Å, $b = 11.9699(8)$ Å, $c = 13.9367(10)$ Å, $\alpha = 66.313(1)°$, $\beta = 71.987(2)°$, $\gamma = 75.144(2)°$, $V = 1712.9(2)$ Å^3, $d_{calc} = 1.553$ g cm^{-1}, space group $P\bar{1}$, $Z = 2$. The intensities of 16610 reflections were measured on an automated Smart 1000 CCD diffractometer at 110 K (Mo-Kα radiation, graphite monochromator, ω scanning technique, $2\theta_{max} = 56°$), and 7444 observed reflections ($R_{int} = 0.0627$) were used in calculations. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic/isotropic displacement parameters against F^2. The hydrogen atoms were revealed from difference electron density syntheses and refined using the riding model. The final reliability factors were as follows: $wR_2 = 0.1008$, GOOF 0.931 for all reflections ($R_1 = 0.0489$ for 4318 reflections with $I > 2\sigma(I)$) All calculations were carried out using the SHELXTL PLUS program package.[35]

Cadmium and zinc complexes 2 and 3 were prepared by refluxing methanolic solutions containing the corresponding ligand **1** (2 mmol) and metal acetate (1 mmol) for 30—40 min. The precipitates that formed were filtered off, washed with ethanol, and recrystallized from a mixture of dichloromethane and hexane. The yields were 60—70%. The NMR spectra are given in Tables 2 and 5.

Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolethiolato]cadmium(II) (2a). The yield was 0.49 g (61%). Found (%): C, 48.27; H, 2.70; N, 15.25. $C_{38}H_{28}CdN_{10}S_2$. Calculated (%): C, 48.43; H, 3.00; N, 15.39.

Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolethiolato]zinc(II) (3a). The yield was 0.47 g (62%). Found (%): C, 48.27; H, 2.70; N, 15.25. $C_{38}H_{28}N_{10}S_2Zn$. Calculated (%): C, 48.43; H, 3.00; N, 15.39.

Bis{3-methyl-1-phenyl-4-[(*E*)-(quinolin-8-ylimino)methyl]-1*H*-pyrazole-5-thiolato}cadmium(II) (2b). The yield was 0.52 g (65%). Found (%): C, 59.97; H, 4.00; N, 14.15. $C_{40}H_{30}CdN_8S_2$. Calculated (%): C, 60.11; H, 3.78; N, 14.02.

Bis{3-methyl-1-phenyl-4-[(*E*)-(quinolin-8-ylimino)methyl]-1*H*-pyrazole-5-thiolato}zinc(II) (3b). The yield was 0.53 g (71%). Found (%): C, 63.27; H, 4.63; N, 14.65. $C_{40}H_{30}N_8S_2Zn$. Calculated (%): C, 63.87; H, 4.02; N, 14.90.

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