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^{15}N NMR SPECTROSCOPY OF 5-(2-HETEROARYL)FORMAZANS AND THEIR ZINC AND CADMIUM CHELATES

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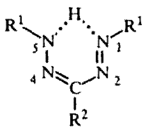
The ^{15}N NMR shifts of 5-heteroarylformazans (Het = 3-chloro-2-quinoxalyl and 2-benzothiazolyl) and their complexes with zinc and cadmium and also some model compounds were measured. Procedures were developed for the use of ^{15}NMR in structural investigations of formazans and their complexes, and the formation of pseudooctahedral bisformazanates with metals of the zinc subgroup was confirmed. The increments of complexation in the chemical shifts of the ^{15}N nitrogens and ^{13}C carbons of the tridentate heteroarylformazans are not independent quantities. There are algebraic combinations of the increments in the chemical shifts that are practically independent of the substitution of the zinc by cadmium, substitution of substituents at the 1-aryl and the meso-carbon atom, and even substitution of the heteroaryl. This property is reminiscent of the analogous relations between the increments of the substituents in such π-conjugated systems as benzene derivatives.

The positions of the ^{15}N NMR lines in the spectra of heteroarylformazans and heteroarylformazanates had not been determined or analyzed until recently. Data on the ^{15}NMR spectra of related compounds (azobenzenes, hydrazones, triazenes) were available, for example, in the numerous papers by Lycka and coworkers [1-7]. Earlier [8, 9, etc.] we established the structure of heteroarylformazans and heteroarylformazanates fairly reliably. In these papers ^1H and ^{13}C NMR were used among other methods for the investigation of the structures.

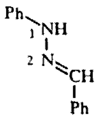
The aim of the present work was to assign the lines in the ^{15}N NMR spectra unambiguously on the basis of a comparison of the NMR data of the investigated and related compounds. Investigation of the ^{15}NMR shifts made it possible to check and confirm our previous ideas about the tautomeric and isomeric form of the heteroarylformazans in solutions.

The assignment of the lines in the ^{15}N NMR spectra and the investigation of the increments of complexation $\Delta^k\delta_N$ to the ^{13}C chemical shifts $\Delta^k\delta_C$ presented an interesting procedural NMR problem, useful for further applications during the investigation of the derivatives of heterocycles, formazans, and finally the coordination compounds of metals of the zinc subgroup. We recall that by the increment $\Delta^k\delta_N$ or analogous increment we mean the difference between the corresponding chemical shifts (in this case δ_N) in the complex and in the initial ligand. We expected and in the course of the work obtained evidence for the uniqueness of the formation of the nitrogen (and carbon) NMR spectra in the conjugated systems of the metal-chelate rings, including chelates containing the individual bonds of a heterocyclic substituent.

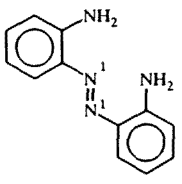
The investigation was started with three symmetrical 1,5-diarylformazans [1,5-diphenylformazan (I), 1,5-diphenyl-3-propionylformazan (II), and 1,5-di-p-tolyl-3-acetylformazan (III)] and also benzaldehyde phenylhydrazone (IV), o,o-diaminoazobenzene (V), and azobenzene (VI) as models (for the structures, see below, the data in Table 1).



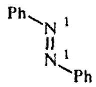
I-III



IV



V



VI

I $R^1 = R^2$ = Ph; II R^1 = Ph, R^2 = COOEt; III R^1 = p-C_6H_4Me, R^2 = COOMe

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TABLE 1. ^{15}N NMR Chemical Shifts on the δ_N Scale (from liquid ammonia) in the Symmetrical Formazans (I-III) and the Model Compounds (IV-VI)

Compound	R^1	R^2	Shifts for N (ppm)	
			$N^{1,5}$	$N^{2,4}$
I	Ph	Ph	312,6	?
II	Ph	COOEt	314,8	400,6
III	p-C_6H_4Me	COOEt	317,5	402,6
IV			144,3	327,2
V			475,9	
VI			508,7	

TABLE 2. ^{15}N NMR Chemical Shifts on the δ_N Scale in the Benzothiazolylformazans (VII-XII) and in the Model Compounds (XIII-XVI)

Compound	R^1	R^2	Shifts and increments for the nitrogens (ppm)				
			N^1	N^2	N^4	N^5	$N^{(3)}$
VII	OMe	Ph	496,1	479,4	291,4	156,6	250,3
VIII	n-Bu	Ph	487,8	482,4	299,6	168,5	254,0
IX	Br	Ph	467,1	477,9	312,1	185,1	?
X	COOMe	Ph	374,4	421,8	364,4	277,9*	278,5*
XI	n-Bu	n-Bu	519,2	474,8	309,6	142,5	239,2
XII	H	n-C_4H_9	519,4	480,8	312,7	145,5	238,5
XIII			465,0*	453,0*	302,1	163,5	$64,7^{NH2}$
XIV					326,4	143,4	241,4
XV					327,4	141,3	237,3
XVI	H	Me	514,6	504,9	377,4*	272,6*	$119,0^{Me}$

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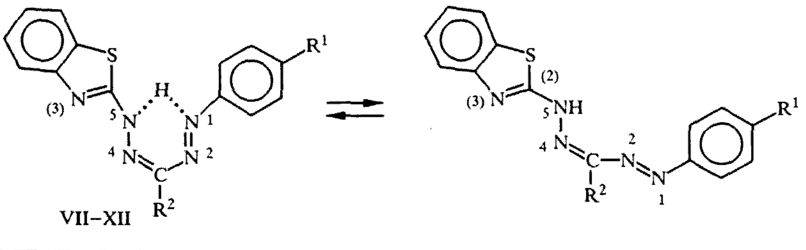
*The assignments may be changed; the shift marked with NH_2 belongs to the NH_2 nitrogen; Me, the shift of the nitrogen at which the substituent is Me.

We then studied the benzothiazolylformazans (VII-XII) and their complexes (M = Zn, Cd):



VII–XII

Compound	R^1	R^2	Compound		R^2
VII, VII_M	OMe	Ph	X, XM	$COOM_e$	Ph
VIII, $VIII_M$	p-Bu	Ph	XI, XI_M	p-Bu	p-Bu
IX, IX_M	Br	Ph	XII XII_M	H	p-Bu

TABLE 3. ^{15}N NMR Chemical Shifts on the δ_N Scale in 3-Chloro-2-quinoxalylformazans and Some Formazanates of Zinc and Cobalt and the Individual Increments of Complexation $\Delta^k\delta_N$ (in parentheses)

Compound	R^1	R^2	Shifts and increments for the nitrogens (ppm)					
			N^1	N^2	N^4	N^5	$N^{(1)}$	$N^{(3)}$ NO_2
XVII^{Pr}	*i*-Pr	NO_2	501,6	487,7	291,4	155,4	273,4	318,2 366,8
XVIII$_{Zn}$	*n*-Bu	OMe	431,2	471,7	258,5	282,2	198,8	315,3
XVIII$_{Cd}$	*n*-Bu	OMe	413,7	467,8	261,7	292,1	204,0	314,0
XIX$^{Bu}{}_{Zn}$	*n*-Bu	NO_2	415,5 (-86,1)	461,6 (-16,1)	270,9 (-20,5)	299,6 (144,0)	207,1 (-66,3)	319,0 (0,8) 366,8 (0,4)
XIX$^{Bu}{}_{Cd}$	*n*-Bu	NO_2	401,6 (-100,0)	458,0 (-29,7)	275,7 (-15,7)	309,9 (154,5)	212,2 (-61,2)	318,3 (0,1) 366,6 (-0,2)

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*Roman numerals represent the ligands; the superscripts, the *para* substituents at ^{1}Ar (R^1); the subscripts, the metals forming the complex. The difference in R^1 was not taken into account during the calculation of $\Delta\delta_N$.

TABLE 4. ^{15}N NMR Chemical Shifts on the δ_N Scale (downfield from liquid ammonia) in the Benzothiazolylformazans and Their Zinc and Cadmium Bisformazanates for the Formazans (VII, VIII, XI, XII) and the Increments of Complexation $\Delta\delta_N$.*

Ligand	R^1	R^2	Shifts and increments for the nitrogens (ppm)				
			N^1	N^2	N^4	N^5	$N^{(3)}$
VII	OCH_3	C_6H_5	496,1	479,4	291,4	156,6	250,3
VII$_{Zn}$ †			403,6 (-93,0)	454,1 (-25,3)	255,3 (-36,1)	302,9 (146,3)	199,4 (-50,9)
VIII	*n*-C_4H_9	C_6H_5	487,8	482,4	299,6	168,5	254,0
VIII$_{Zn}$			402,3 (-85,5)	460,7 (-21,7)	259,5 (-40,1)	308,0 (139,5)	201,1 (-52,9)
VIII$_{Cd}$ †			394,3 (-93,5)	460,6 (-21,8)	264,7 (-34,9)	313,1 (144,6)	202,7 (-51,3)
XI	*n*-C_4H_9	*n*-C_4H_9	519,2	474,8	309,6	142,5	239,2
XI$_{Zn}$			451,0 (-68,2)	470,8 (-4,0)	253,3 (-56,3)	312,4 (169,9)	190,2 (-49,0)
XI$_{Cd}$ †			408,0 (-111,2)	460,6 (-14,1)	256,6 (-53,0)	312,3 (169,8)	199,6 (-39,6)
XII	H	*n*-C_4H_9	519,4	480,8	312,7	145,5	238,5
XII$_{Zn}$			446,5 (-72,9)	471,7 (-9,1)	252,6 (-60,1)	311,0 (165,5)	190,0 (-47,6)
XII$_{Cd}$ †			427,7 (-91,7)	464,7 (-16,1)	260,1 (-52,1)	314,6 (169,1)	200,9 (-37,6)

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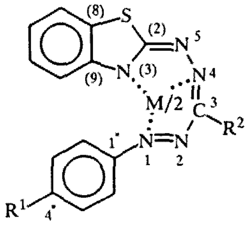
*The values of the increments are given in the rows containing the shifts of the complexes in parentheses.

†With the addition of $Cr(acac)_3$. The change of $\Delta\delta_N$ for 10 mg/cm^3 is less than 3 ppm for the complexes of (XI) and (XII) with cadmium and up to 5 ppm for the complex of (XI) with zinc.

TABLE 5. ^{13}C NMR Increments of Complexation $\Delta\delta_C$ in the Shifts of Some of the Carbons in the Ligand for Zinc and Cadmium Bisbenzothiazolylformazanates

Compound	R^1	R^2	Increments for the carbons (ppm)				
			C^3	$C^{(2)}$	$C^{(9)}$	$C^{(4)}$	$C^{4'}$
VII_{Zn}	OMe	Ph	1,3	12,9	-3,8	-3,2	-2,0
$VIII_{Zn}$	*n*-Bu	Ph	1,7	12,5	-2,7	-3,4	-2,5
$VIII_{Cd}$	*n*-Bu	Ph	2,1	12,9	-2,5	-3,3	-2,4
XI_{Zn}	*n*-Bu	*n*-Bu	4,8	13,1	-1,7	-3,5	-1,1
XI_{Cd}	*n*-Bu	*n*-Bu	1,1	13,8	-2,4	-3,0	-2,6
XII_{Zn}	H	*n*-Bu	5,2	13,2	-4,3	-3,2	-1,7
XII_{Cd}	H	*n*-Bu	1,5	13,8	-3,1	-2,5	-1,9

The complexes of the formazans have the following structure [for data on the chemical shifts of the formazans (VII-XII), see Table 2]:

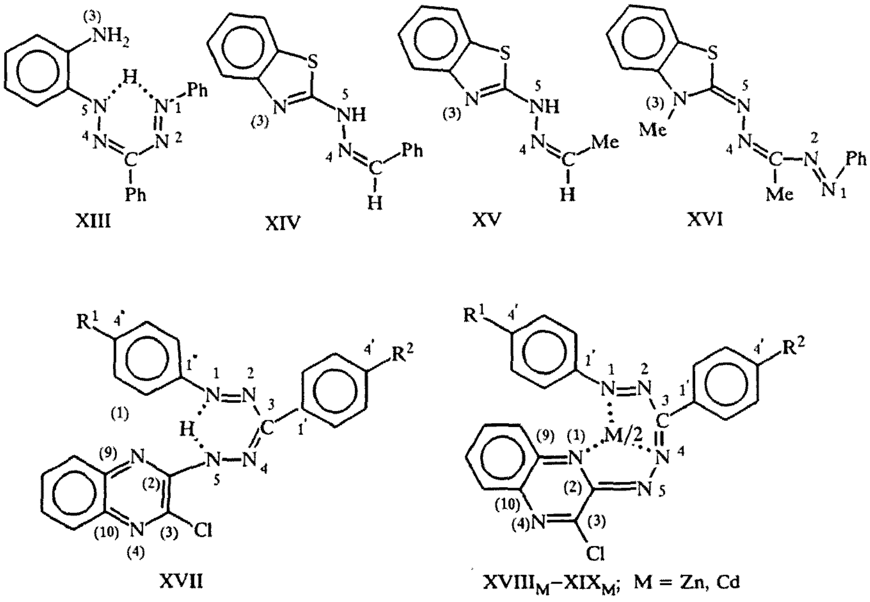


VII_M–XII_M; M = Zn, Cd

As model compounds we used the following (see the scheme): 1-(2-aminophenyl)-3,5-diphenylformazan (XIII) analogous with reference to positions 3 and 5 [a 0.15 M solution in the presence of $Cr(acac)_3$]; benzaldehyde 2-benzothiazolylhydrazone (XIV) and acetaldehyde 2-benzothiazolylhydrazone (XV) analogous with reference to position 5; finally, as a model of the tautomeric imino form, 1-phenyl-3-methyl-5-(3-methyl-2-benzothiazolylidene)formazene (XVI), which according to the ^{13}C NMR data has the *anti*-s-*trans* configuration (see also the data in Table 2).

The ^{15}N chemical shifts of 3-chloro-2-quinoxalylformazan (XVII) and the complexes of the analogous formazans (XVIII, IX) measured in the present work are given in Table 3.

Scheme



XVII R^1 = *i*-Pr, R^2 = NO_2; XVIII R^1 = *n*-Bu, R^2 = OMe; XIX R^1 = *n*-Bu, R^2 = NO_2

TABLE 6. ^{13}C NMR Increments of Complexation $\Delta^k\delta_C$ in the Shifts of Some Carbons in the Ligand for Zinc and Cadmium Bisquinoxalylformazanates*

Compound	Increments for the carbons (ppm)							
	C^3	$C^{(2)}$	$C^{(3)}$	$C^{(6)}$	$C^{(8)}$	$C^{(9)}$	$C^{(10)}$	$C^{4''}$
$XIX^{Bu}{}_{Zn}$	3,2	10,1	10,0	-5,9	-1,3	-2,4	-1,2	-2,0
$XIX^{Bu}{}_{Cd}$	3,3	9,9	11,1	-5,3	-1,1	-2,4	-0,7	-1,6

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*The increments of complexation in the shifts of formazanates with a butyl para substituent are measured in relation to the shifts of the formazans (XVII) with an isopropyl para substituent in R^1 (the difference in R^1 is not taken into account during the calculation of $\Delta\delta_C$). The Roman numerals represent the ligands, the superscripts represent the para substituent at R^1, and the subscripts represent the metals forming the complexes.

TABLE 7. Mean Values of the Increments of Complexation of the Nuclei of the Ligand at Identical Positions (i) $\langle I_{N,C}\rangle_i = (\Delta^k\delta_{C,N})_i$ Among the Nine Investigated Complexes and the Mean-Square Deviations of These Values q_i. The Numbering of the Positions of the Nitrogens and Carbons $(N,C)_j$ Corresponds to That Indicated in the Schemes for (VII-XI) and (XVIII, XIX).

The atom to which the nucleus belongs	$\Delta^k\delta_{C,N}$	q_i
N^1	-89,1	±12,3
N^4	-41,1	±14,9
$N^{(1\text{ or }3)}$	-50,7	±8,6
N^2	-17,5	±7,6
N^5	155,9	±12,0
C^3	2,7	±1,4
$C^{(2)}$	12,5	±1,2

Unfortunately, these data are incomplete. For the formazan (XVIII) the nitrogen shifts were only measured in complexes with zinc and cadmium (but not with formazan itself!), while the formazan (XVII) serves as model for calculation of the increments in the complex of the formazan (XIX), which differs in the substituent at the *para* position at N^1 (isopropyl instead of n-butyl).

The concluding stage of the present work included investigation of the benzothiazolylformazanates of the metals and determination of the increments of complexation for various ligands. The results of this investigation are given in Table 4, which also gives data on the increments of complexation for the quinoxalylformazanates given in Table 3. The schematic structure of the bisheteroarylformazanates (VII_M-XII_M) (M = Zn, Cd) is supported by the present investigation. A discussion of the results presented in Tables 1-4 follows. See the experimental section for some of the procedural details.

The use of ^{15}N NMR structural investigations has always been considered promising, frequently giving more direct evidence than ^{13}C NMR for the presence or absence of one or the other structural element (e.g., [10]). In particular, the possibilities of natural-abundance ^{15}N NMR have increased with improvements in the sensitivity and the range of technical resources in modern NMR spectroscopy [11].

In the *syn*-s-*cis* configuration the hydrogen at N^5 forms an intramolecular hydrogen bond with the N^1 nitrogen. In the symmetrical formazans (I-III) the ^{15}N NMR spectra are degenerate, and the shifts of the N^1, N^5 and N^2, N^4 pairs coincide. The shifts of the inner nitrogens of the chain are almost 100 ppm larger than those of the outer nitrogens. As shown by the spectra of (V, VI), the nitrogens of azobenzenes are descreened much more strongly than the inner nitrogens of the arylformazans, while the shift of the nitrogen with the CH(Ph) substituent in the phenylhydrazone (IV) falls in the same range as the shifts of N^1 and N^5 in the symmetrical formazans, whereas the NH(Ph) nitrogen is comparatively strongly screened (Table 1). It can be supposed that the aryl substituents in the molecules of the formazans have a donating effect and are conjugated better with the nitrogen atoms if the latter participate in an intramolecular hydrogen bond. In any case the data in Table 1 make it possible to determine the range of the chemical shifts of the nitrogens in the formazan chain and then to identify the lines of the nitrogens in the heterocycle.

Some information on the structure of heteroarylformazans can be extracted from the data in Table 2. It must be borne in mind that the conformation of the formazans (VII, VIII) (clearly *syn*-s-*cis*) and the intramolecular hydrogen bond leads to a shift in the order of 14 ppm for their protons. At the same time in the given formazans the H is shifted somewhat toward N^5, and the shifts of N^1 are accordingly closer to the "azobenzene" shifts (about 500 ppm from liquid ammonia), while the shifts of N^5 (at which there is a heteroaryl substituent) are appreciably smaller (150-200 ppm on the same scale) than for the terminal nitrogens of the symmetrical diphenylformazans. However, the approach of the lines of these nitrogens in one of the formazans (to 374.4 and 277.9 respectively) does not necessarily indicate a relatively stronger hydrogen bond in this compound (X), i.e., an increase in the contribution from or the preponderance of the *syn*-s-*cis* configuration, but rather conjugation between the formazan chain and the *para*-acetyl substituent at 1-Ar. The $N^{(3)}$ nitrogen of the heterocycle has a line in the region of 235-275 ppm on the same scale. Only in one case [compound (X)] does its line coincide in shift with the line of the terminal nitrogen atom of the formazan chain N^5, and it is the shift of the latter that is anomalous. We note that the data on this compound are not entirely reliable in so far as all the shifts of the nitrogens in compound (X) differ from the typical values for compounds (VII, VIII, XI, XII) and even (IX).

According to the PMR data, the formazans (XI) and (XII) are assumed to be in the *syn*-s-*trans* configuration, and the hydrogen is probably localized almost completely at N^5 (the screening of the latter is maximum in these compounds). The screening of the $N^{(3)}$ nitrogens is also maximum in these compounds (shift about 235-240 ppm).

Comparison with the model compounds (XIII-XVI) (particularly with the last compound, which has the tautomeric imino form) makes it possible primarily to confirm the heteroarylhydrazone form of the investigated formazans (VII-XII) on the basis of δ_N values.

The NMR data of the nitrogen in the bisformazanates in comparison with the NMR in the formazanates themselves (i.e., data on the increments of complexation $\Delta^k\delta_N$) make it possible to verify sufficiently confidently and moreover sufficiently graphically the expected type of coordination and the change in the tautomeric form of the ligand during complexation. The structure of the complex, shown diagrammatically in the formulas (VII_M-XII_M), agrees well with the NMR of the nitrogen (and also with the previous NMR data of carbon [8, 9]).

First, the principal change in the shift of the N^5 (descreening by 140-170 ppm) during complexation corresponds to the change of the ligand in the complex into the imino form and the formation of the $N^5{=}C^{(2)}$ double bond. Together with the formation of the coordination bond such an effect will lead to the appearance of an additional and appreciable shift (-37 to -53 ppm) of $N^{(3)}$ in the complex. The same effect for $N^{(1)}$ in the quinoxalylformazanates is stronger and exceeds 60 ppm in absolute value. Here and below (and also in the tables) the numbering in parentheses refers to the atoms of the heteroaryl, and that without parentheses refers to the formazan chain.

Second, the terminal nitrogen N^1 undergoes strong screening during complexation ($\Delta^k\delta_N$ in the order of 70-110 ppm). The increments in the shifts of all the other coordination units are somewhat smaller for complexation with zinc and appreciably smaller for complexation with cadmium. However, all these increments are negative (correspond to screening, i.e., to increase in the symmetry of the environment of the nitrogen [10]).

Third, the increment of N^2 is comparatively small and has a negative sign. It is interesting (see below) that if we seek the on average linear (algebraic) combination of $\Delta^k\delta_N$ closest to zero, it is necessary in this combination to take the increment for N_2 with reversed sign, like the increment at the *para* position with substitution by strong π-donating or π-accepting groups (it also includes the increment $\Delta^k\delta_C$ with reversed sign and the increment for $C^{(2)}$ with positive sign — seven values in all). This provides qualitative evidence for the determining role of conjugation in the change of the shifts of the N^2 and C^3 nuclei during complexation.

All that has been said about the ^{15}N NMR of benzoylthiazolylformazans and bisbenzothiazolylformazanates also holds qualitatively for their quinoxalyl analogs (see the data in Table 3). As we have already pointed out, the data in Table 3 are too fragmentary to discuss them in detail. It is, however, possible to discuss the data on the $\Delta^k\delta_N$ values jointly for both types of formazanates. In addition, Tables 5 and 6 give the values of the increments of complexation in ^{13}C NMR for benzothiazolyl- and quinoxalylformazanates respectively. Here the positions of the carbons important to us are singled out: in particular, in addition to the meso-carbon C^3 and some of the $C^{(i)}$ atoms of the heteroaryl (in accordance with the numbering in the schemes) there are the carbons of the aryl substituent at $C^3-C^{k'}$ marked with a single prime and the aryl at $N^1-C^{k''}$. It is easy to see (this was confirmed by checking the correlation coefficients between the series of data) that as a result of the too widely varying and fairly numerous differences in the structure of the ligand and in the electronic characteristics of the substituents (e.g., in the values of the Hammett constants) and also as a result of the difference in the complex-forming metals there is no correlation between the series of increments in the shifts of the various C and N atoms. It is possible, it is true, to see a clear correlation between the increments in the shifts of $C^{4''}$ and N^1 in a small amount of the data (four complexes). (The increments in the shifts of C^3 and $C^{1',4'}$ vary too little in the series of investigated complexes, while the increments in the shifts of $C^{(2)}$ are small in absolute value.)

We would also like to draw attention to the fact that the appearance of conjugation effects in metal chelate rings was first noticed by Ryabokobylko in the case of the effect of the size of the metal chelate ring on the ^{13}C chemical shifts of an aromatic ring coupled with the chelate [8, 12]. In relation to the results in [12] the present work represents a development in two directions: first, two types of structures (with the participation of one of the atoms of the heterocycle in coordination) were considered; second (and most important), data on the NMR of the nitrogens (primarily the nuclei belonging to the coordination points) were used for the structural investigations.

In the search for characteristic analytical features of complexation we give below certain other relations in the observed $\Delta^k\delta_N$ values, which we examine in conjunction with or in comparison with $\Delta^k\delta_C$.

1. DIFFERENCES IN THE INCREMENTS IN COMPLEXES WITH VARIOUS STRUCTURES

These differences are small. Nevertheless, it can be seen that:

a) For the N^1 nitrogen in the complex of the same ligand with cadmium the increments are larger in absolute value than in the complex with zinc; the $\Delta^k\delta_{N1} - \Delta^k\delta_{N2}$ values differ even more significantly (in favor of the cadmium complexes) (20-40 ppm larger in the cadmium complexes). This relation holds not only for all three pairs of complexes with identical ligands but also in general for any complex of zinc in comparison with the cadmium complexes.

b) The $\Delta^k\delta_{N5} - \Delta^k\delta_{N3} - \Delta^k\delta_{N4}$ value depends in a characteristic way on the substituent at the meso-carbon atom C^3. It acquires values in the range of 225-240 ppm for phenyl and 260-280 ppm for alkyl substituents.

c) The shift during complexation of the nitrogen coordinating the metal in the heterocycle $\Delta^k\delta_{N(1,3)}$ is 25-30% larger for the quinoxalyl nitrogen $N^{(1)}$ than for the benzothiazolyl nitrogen $N^{(3)}$.

2. INCREMENTS IN EACH OF THE INVESTIGATED SHIFTS (AMONG THEM THE TWO CARBONS C^3 AND $C^{(2)}$) ARE COMPARATIVELY CLOSE FOR ALL NINE INVESTIGATED COMPLEXES.

This fact is illustrated by the data in Table 7, which gives the arithmetical means of the increments for all nine complexes in each of the seven investigated shifts. (The respective notation $I_{(N,C)j} = \Delta^k\delta_{Nj}$ is used for the mean value $\langle I_{(N,C)}\rangle_j$ in this table.) The table also gives the mean-square deviations (MSD) of each of the increments from the mean values:

$$q_j = \sqrt{\Sigma\, I(N,C)_j - <I(N,C)>j)^2/9} \quad .$$

Certain linear (algebraic) combinations of a few increments are particularly close to each other, e.g., for the algebraic sums of the increments of complexation averaged among nine complexes for all seven nuclei entering into the conjugated metal chelate rings formed during the coordination of the metal:

$$<I_{\mathrm{N}1} - I_{\mathrm{N}2} - I_{\mathrm{C}3} + I_{\mathrm{N}4} + I_{\mathrm{N}5} + I_{\mathrm{C}(2)} + I_{\mathrm{N}(1,3)}> = (2{,}0 \pm 7{,}8)\ \mathrm{ppm},$$

where the increments in the shifts of the N^2 atom and the meso-carbon are taken with negative sign. For normally distributed independent values the MSD would be approximately ±22 ppm. The variation of the individual signs of the increments in a "balanced" linear combination is reminiscent of the situation, let us say, for the increments of strong π-donating and π-accepting substituents in the benzene ring, where in the analogous combination it is necessary to use a negative sign at the *para*-increment. (From the corresponding data [13] it is seen that the MSD here is +3.45 instead of +11.) Thus, it is clear that such relations are characteristic of conjugated systems. For instance, it was shown in [14] that there are correlations for the increments of the substituents in the benzene rings with full charge, calculated by the CNDO SCF method, and for the increments in the shifts of hydrogens even with π-charges, calculated by the even simpler Hückel method (HMO). The MSD of these values are characterized by the same effects as for the investigated increments of complexation. (We have already published the remarks made here in [15].)

The mean of the sum of three increments in the shifts of the nuclei of the coordination points (CP) is also an almost constant quantity for all the investigated complexes (with various metals, heteroaryls at position 5, and substituents in the side chains):

$$<I_{\mathrm{N1}} + I_{\mathrm{N4}} + I_{\mathrm{N(1,3)}}> = -180{,}5 \pm 8{,}9,$$

whereas the MSD for normally distributed independent values would amount to ± 21.1. The formation of the metal chelate rings and the presence of conjugation effects in them, including those with the participation of the orbitals of the metals, follows from the simplified arguments presented below.

The structure of the bis-5-(2-heteroaryl)formazanates investigated in the present work is octahedral both in the crystal and in the solution. The doubly charged ions of the zinc group, which include Hg^{2+}, Cd^{2+}, and Zn^{2+}, have completely filled upper *d* shells (5*d*, 4*d*, and 3*d* respectively). In the monograph [16] (pp. 110, 111), which has become almost classical, the relationships governing the formation of the molecular orbitals, including both the orbitals of the central ion and linear combinations of the orbitals of the coordination points, are examined. According to the standard nomenclature used in this monograph, for an octahedral environment the atoms coordinating the metal are numbered from 1 to 6, and in the system of coordinates associated with the metal atoms 1 and 4, for example, lie along the z axis, atoms 3 and 6 lie along the x axis, and atoms 2 and 5 lie along the y axis. Thus, in our case of a biscomplex of a tridentate ligand points 1, 2, and 3 belong to one of the ligands, say α, while points 4, 5, and 6 belong to the other (β). The local systems of coordinates (for each of the coordination points) were chosen in such a way that their z axes were directed along the metal–ligand bond, while the x and y axes of each next point in number were perpendicular to the like axes of the local system of the previous one. (The same holds for points 6 and 1.)

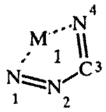
This demonstrates the antisymmetry (symmetry from the standpoint of the sign) of the contributions from the π-orbitals of the individual coordination points to the expressions for the π-type MO; for example, for the pair $\pi_{1x,y}$ and $\pi_{4x,y}$ and so forth and, on the other hand, in the transition from one MO to another of similar symmetry either the signs alone change, or the local axes alone change, or both change simultaneously. Specifically what changes depends on the type of symmetry.

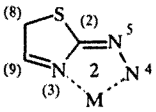
It is clear that approximately one unit of negative charge is transferred from the M^{2+} ion to the N^1 atoms of each of the two ligands and the bonds of the metal with $N^{1\alpha,\beta}$ are partially ionic. An almost completely symmetrical MO with a linear combination of the σ-orbitals of all six coordination points (symmetry group A_{1g}) is then formed by the six σ-orbitals of the central ion. The antisymmetric π-MOs of the metal belong to the T_{1u} group and form π-bonds with the π-orbitals of each symmetrically arranged (in relation to the metal) pair of coordination points of the various ligands.

Molecular orbitals of the T_{2g} type fully symmetrical with reference to all the π-orbitals are formed with the participation of the so-called $d\gamma$-orbitals: d_{xy}, d_{yz}, and d_{zx}. The overall MO of such a type is fully symmetrical with respect to any permutations of the coordination points.

The formation of a MO of the E_g type with the participation of the two so-called d_ε orbitals of the metal ($d_{(3z^2-r^2)}$, $d_{(x^2-y^2)}$) undoubtedly leads to a symmetry reduction. In this case it is logical to expect the appearance of an isolated Z axis, which may be directed along the $N^{4\alpha}-M-N^{4\beta}$ or $N^{(1,3)\alpha}-M-N^{(1,3)\beta}$ line (the superscripts α and β in this case refer to the various ligands), since a smaller density of charge is expected at the $N^{4\alpha,\beta}$ nitrogens and at the nitrogens of the heterocycle (in the case of benzothiazolylformazans, at $N^{(3)\alpha,\beta}$). (Electronic charge is transferred from the metal to the terminal nitrogen N^1, and the corresponding bonds are elongated, i.e., are less covalent.) A further qualitative argument in favor of the special position of the N^4 point in the complex follows from the data from x-ray crystallographic analysis (see below). In the monograph [16] it is suggested that the MOs must be arranged in the following order of increasing energy: 1) A_{1g} with the participation of the σ-orbitals of the metal; 2) T_{1u} with the participation of the π-orbitals of the metal; 3) E_g with the participation of the d_ε orbitals of the metal (bonding orbitals); 4) T_{2u} nonbonding (with the participation of the d_γ orbitals of the metal).

Almost all the orbitals of the metal (except those belonging to the A_{1g} group) thus participate in the π-system of the metal chelate rings; in these complexes there are two such rings, and both are five-membered. One chelate ring (1) contains the metal M, the nitrogen N^4, the carbon C^3, and the nitrogens N^2 and N^1, while the other (2) contains the metal M, the nitrogen of the heterocycle $N^{(Het)}$, the carbon of the heterocycle $C^{(2Het)}$, the nitrogen N^5, and the nitrogen N^4.





We note that in this way we obtained the total number of the atoms the increments in the chemical shifts of whose nuclei we considered above (seven, not including the metal). Although in [17] we measured the increments of the substituents in the chemical shifts of ^{111,113}Cd, this was done for the complexes of other ligands, and we were deprived of the possibility of carrying our primitive but probably not meaningless analysis to the logical conclusion (to take account of the increments of the substituent in the shift of the metal).

The results from x-ray crystallographic analysis of the bisheteroarylformazanates serve to confirm that conjugation plays a significant role in the electronic structure of the investigated complexes (e.g., see [18, 19]). The planar structure of the ligands and the chelate rings demonstrates unambiguously the presence of conjugation in the structure of the ligand and the metal chelate ring. Here, however, the distortion of the coordination octahedron is so large that specialists on structural analysis are already talking about a trigonal antiprism and not an octahedron. Nevertheless, the qualitative arguments presented above remain in force. The N^4-M and $N^{(1,3)}-M$ bonds are actually much shorter than the N^1-M bond, but in practice only the $N^{4\alpha}-M-N^{4\beta}$ triangle degenerates to a straight line, while the other pairs of coordination bonds have angles of 110 to 126° between them.

EXPERIMENTAL

The quinoxalylformazans and their complexes (quinoxalylformazanates) studied in the present work were synthesized and supplied to us by M. N. Stopnikova, while the benzothiazolylformazanates and the model compounds were supplied by G. N. Lipunova and coworkers (Urals Pedagogical Institute).

The methods for the synthesis of the investigated ligands and complexes were described in [8,9]. The preliminary results of the investigations described in the present work were reported in [20] and in the abstracts [21-23]. The measurements in the present work were made by S. G. Sakharov on a Bruker MSL-300 instrument. The investigated samples were as a rule 0.015-0.025 M solutions in deuterochloroform and were sealed into 10-ml tubes. The DEPT, INEPT, and other methods that have proved extremely effective in other cases [11] could not be used for the investigated samples on account of the absence of appreciable spin–spin coupling constants $^{n>2}J_{N-H}$ and the presence of fairly rapid intermolecular proton–proton exchange between the $N^{5,1}$ nitrogens but mostly on account of the low concentration of the complexes. The spectra were record by pulsed excitation with Fourier transformation. In almost all cases (with the exception of isolated compounds) irradiation of H^1 was dispensed with, and extremely long experiments were used (8-15 h). In some cases it was necessary to add to the solution appreciable amounts (10 mg in 1 ml) of the relaxation agent Cr(acac)$_3$, without which the necessary sensitivity could not be achieved. The chemical shifts were determined either on the absolute scale, with calibration of the instrument, or with an external standard [a detachable tube with NO_3^- in an aqueous solution ($\delta_{N\cdot}$ = 383)].

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REFERENCES

1. A. Lycka, Coll. Czech. Chem. Commun., **47**, 1112 (1982).
2. A. Lycka, Coll. Czech. Chem. Commun., **48**, 3104 (1983).
3. V. Machacek and A. Lycka, Coll. Czech. Chem. Commun., **49**, 244 (1984).
4. A. Lycka and P. Vetesnik, Coll. Czech. Chem. Commun., **49**, 963 (1984).
5. A. Lycka, T. Liptai, and J. Jirman, Coll. Czech. Chem. Commun., **52**, 727 (1987).
6. A. Lycka, J. Prakt. Chem., **331**, 11 (1989).

7. L. A. Fedorov, A. Lycka (A. Lychka), and J. Irman, Izv. Akad. Nauk. Ser. Khim., No. 11, 2530 (1989).
8. L. V. Shmelev, M. N. Stopnikova, Yu. S. Ryabokobylko, A. V. Kessenikh, I. A. Krol', B. V. Zhadanov, V. M. Agre, T. V. Chernysheva, and V. M. Dziomko, Koordinats. Khim., **15**, 1027 (1989).
9. L. V. Shmelev, A. V. Kessenikh, E. E. Orlova, I. N. Polyakova, Z. A. Starikova, G. N. Lipunova, N. B. Ol'khovikova, and L. I. Rusinova, Khim. Geterotsikl. Soedin., No. 9, 1268 (1991).
10. G. I. Martin, M. L. Martin, and I. P. Goiouesnard, ^{15}N NMR Spectroscopy, Springer Verlag, Berlin (1981).
11. E. Deroum, Modern Methods of NMR for Chemical Investigations [Russian translation], Yu. A. Ustynyuk (ed.), Mir, Moscow (1992).
12. Yu. S. Ryabokobylko and L. V. Shmelev, Koordinats. Khim., **14**, 1179 (1988).
13. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York (1972).
14. P. Lazzaretti and F. Taddei, Org. Magn. Reson., **3**, 283 (1973).
15. A. V. Kessenikh and L. V. Shmelev, Second All-Russia Seminar on "Advances in NMR in Structural Investigations." Abstracts: NMR News in Letters [in Russian] (1995), p. 50.
16. I. B. Bersuker, Electronic Structure and Properties of Coordination Compounds [in Russian], Third edition revised, Khimiya, Leningrad (1986).
17. A. V. Kessenikh and L. V. Shmelev, Khim. Geterotsikl. Soedin., No. 9, 1280 (1995).
18. I. A. Krol', V. M. Agre, L. V. Shmelev, and M. N. Stopnikova, Koordinats. Khim., **14**, 259 (1958).
19. T. G. Takhirov, Yu. I. Aleksandrov, G. N. Lipunova, L. I. Rusinova, N. A. Klyuev, O. A. Kozina, O. A. D'yachenko, and L. O. Atovmyan, Zh. Obshch. Khim., **59**, 2362 (1989).
20. L. V. Shmelev and A. V. Kessenikh, Report on "The Development of Methods of Diagnosis of Reagents and Specially Pure Materials with the Aim of Improving their Methods of Production." Directive 1 [in Russian], All-Union Scientific-Research Institute of Chemical Reagents and Specially Pure Chemicals IREA (Minneftekhimprom) (1990).
21. L. V. Shmelev, A. V. Kessenikh, G. N. Lipunova, and L. I. Rusinova, Sixth All-Union Conference. Abstracts [in Russian], Krasnodar (1990), p. 55.
22. L. V. Shmelev and A. V. Kessenikh, Third All-Union Seminar-School on "The Application of the NMR Method in Chemistry and Petrochemistry." Abstracts [in Russian], Volgograd (1990), p. 12.
23. L. V. Shmelev and A. V. Kessenikh, Tenth All-Union Conference on "Physical Methods in Coordination Chemistry." Abstracts [in Russian], Kishinev (1990), p. 183.