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CHEMICAL SHIFTS AND SPIN–SPIN COUPLINGS OF THE METAL NUCLEI WITH THE CARBON ^{13}C NUCLEI IN THE LIGAND IN MERCURY AND CADMIUM BISHETERO-ARYLFORMAZANATES

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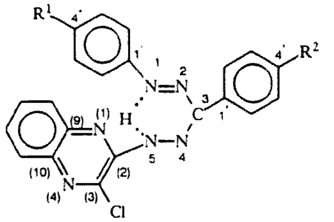
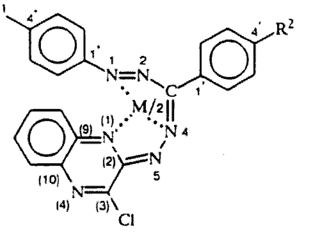
The bis-5-(2-heteroaryl)formazanates of mercury and cadmium ML_2 (where L = 5-quinoxalyl- or 5-benzothiazolylformazanate), having a pseudooctahedral structure, were studied by ^{13}C, ^{199}Hg, and ^{113,111}Cd NMR methods. The ^{199}Hg and ^{113,111}Cd NMR chemical shifts and also the spin–spin coupling constants of these nuclei with the ^{13}C nuclei of the ligands were measured. The results of the experiments indicate π-conjugation in the metal chelate rings of the complexes, including the ring containing the atoms of the heterocycle, and also participation of the f orbitals of the mercury with various symmetry groups in the formation of a π-type MO, leading to different types of transmission of coupling through the various coordination points. The ^{199}Hg and ^{111,113}Cd chemical shifts were also measured for the respective mercury and cadmium complexes.

The objects of the present investigation were the initial 5-quinoxalylformazans (I-VII), 5-benzothiazolylformazans (VIII-XII), and the corresponding mercury (I_{Hg}-VI_{Hg}) and cadmium (I_{Cd}-XII_{Cd}) formazanates. (For the initial investigations of the NMR spectra and structures of 5-quinoxalylformazans, see [1], and for the 5-benzothiazolylformazans and 5-benzothiazolylformazanates, see [2].) General methods for the synthesis of the investigated ligands and complexes were described in [1, 2]. All the quinoxalylformazans and their complexes (the quinoxalylformazanates) were synthesized and supplied to us by M. N. Stopnikova, while the benzothiazolylformazanates were supplied by G. N. Lipunova and coworkers. (The benzothiazolylformazans were studied earlier by the ^{13}C NMR method [2].)

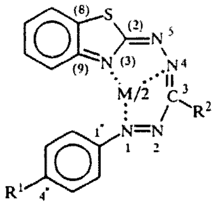


I-VII



I_M–VII_M; M = Hg, Cd

I R^1 – N(Me)$_2$, R^2 – OMe; II R^1 – *n*-Bu, R^2 – OMe; III R^1 – H, R^2 – OMe; IV R^1 – *n*-Bu, R^2 – H; V R^1 – R^2 – H; VI R^1 – *n*-Bu; R^2 – NO$_2$; VII R^1 – H, R^2 – NO$_2$;



$VIII_M$–XII_M, M = Cd

VIIICd R^1 – OMe, R^2 – Ph; IXCd R^1 – *n*-Bu, R^2 – Ph; XCd R^1 – R^2 – *n*-Bu; XICd R^1 – H, R^2 – *n*-Bu; XIICd R^1 – Me, R^2 – *i*-Pr

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TABLE 1. Spin–Spin Coupling Constants of the Nuclei of the Metal Atoms $^{199}Hg/^{113}Cd$ with the Corresponding ^{13}C Carbon Atoms of the Ligand in the Mercury/Cadmium Bisquinoxalylformazanates with Identical Ligands (Hz)

Ligand	Positions of carbon atoms					
	$C^{(2)}$	$C^{(9)}$	$C^{(10)}$	C^3	$C^{1'}$	$C^{1''}$
I	141/33	39/10	21/?	141/52	61/12	22/12
II	137/34	38/10	22/8	140/49	56/12	21/16
III	132/34	40/10	22/9	144/50	56/11	18/15
IV	140/34	38/9	21/7	144/51	54/10	23/15
V	136/33	39/?	20/?	142/52	?/8	21/15
VI	136/33	36/9	24/7	160/?	52/10	27/15
VII	—/33	—/9	—/7	—/52	—/10	—/15

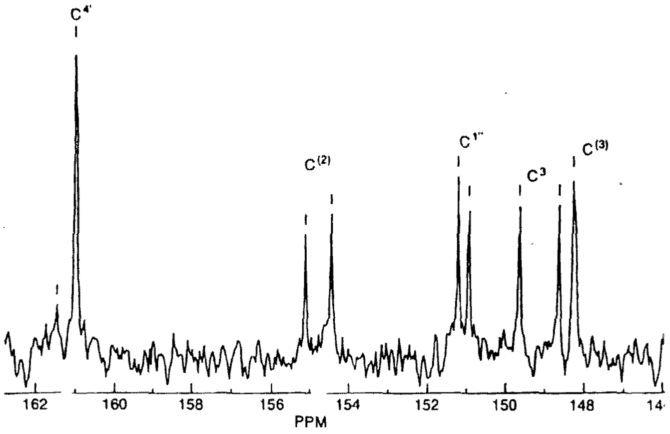


Fig. 1. Part of the ^{13}C NMR spectrum of cadmium bisquinoxalylformazanate with the ligand III enriched in the ^{111}Cd isotope. The chemical shifts on the δ_C scale and the assignments (including the doublets formed during coupling with the ^{111}Cd nucleus) are given.

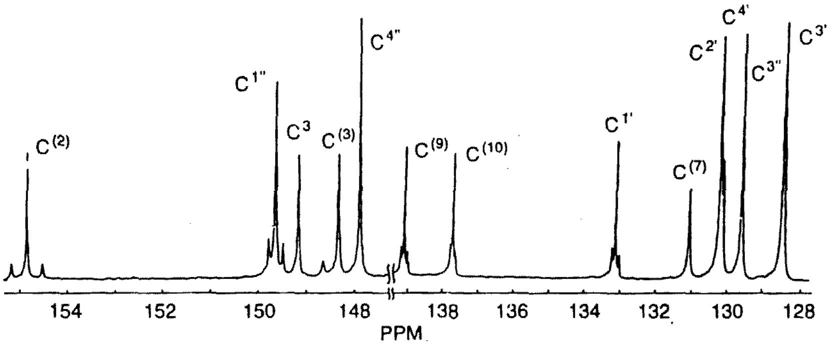


Fig. 2. Part of the ^{13}C NMR spectra of cadmium bisquinoxalylformazanate with the ligand IV (in the ranges of 128-139 and 148-155 ppm). the chemical shifts on the δ_C scale and the assignments of the lines are given. The satellites due to coupling with the $^{111,113}Cd$ isotopes are clearly seen in six of the lines. The downfield satellites only overlap with the $C^{1''}$ in the line of C^3 (at about 149 ppm).

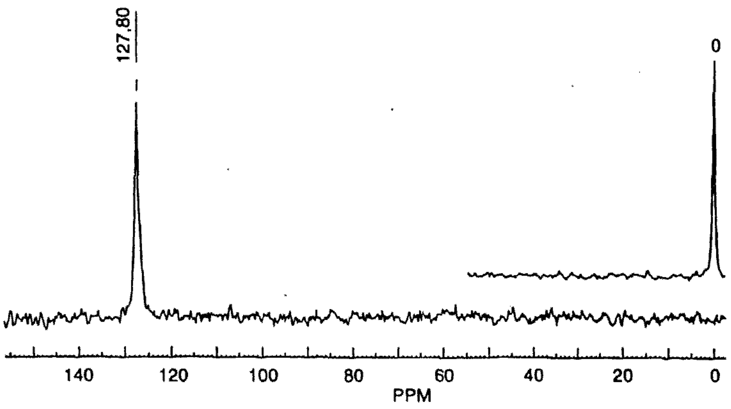


Fig. 3. The ^{113}Cd spectrum of cadmium bisquinoxalylformazanate with the ligand II. The spectrum of the standard sample (an aqueous solution of cadmium chloride).

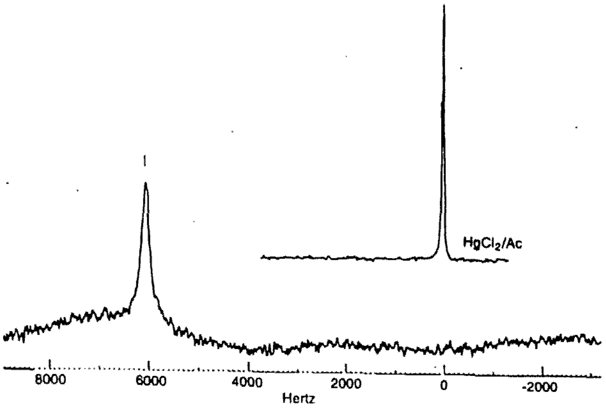


Fig. 4. The ^{199}Hg NMR spectrum of mercury bisquinoxalylformazanate with the ligand VI. The spectrum of the standard sample (a solution of mercuric chloride in acetone).

Mercury has two magnetic isotopes, but only one of them ^{199}Hg has nuclear spin $I = ½$ and can be used for NMR mass measurements. The working frequency of ^{199}Hg in the same polarizing field is 17.83% of the PMR frequency, while the natural abundance of the ^{199}Hg isotope is 16.8%. In the light of these factors the relative sensitivity at the natural abundance amounts to 1.8, if the sensitivity of ^{13}C with the natural abundance in the presence of the proton–carbon nuclear Overhauser effect (an increase of three times during irradiation of the protons) is taken as unity. Cadmium has two "twin" isotopes ^{111}Cd and ^{113}Cd with spins of ½ and with gyromagnetic ratios extremely close in absolute values (negative) (NMR working frequencies are 21.205% of the PMR frequency for ^{111}Cd and 22.182% for ^{113}Cd). The natural abundances of the isotopes are also close (12.75% for ^{111}Cd and 12.26% for ^{113}Cd). By virtue of this the spectral splittings between the satellites in the ^{13}C NMR spectrum, let us say, from ^{111}Cd and ^{113}Cd differ by only 4.7%, while the relative sensitivity in the natural abundance (about 2.5% in relation to the ^{13}CNMR spectrum with the natural abundance and with proton decoupling) is 5.4% higher for ^{113}Cd than for ^{111}Cd (these data can, for example, be found in [3-5]).

One of the complexes of cadmium with quinoxalylformazan (III) (see below, Table 1) was obtained with 100% enrichment with the ^{111}Cd isotope. Therefore, the search for and detection of satellites in the carbon spectrum were based on the conclusive results obtained on the enriched sample (Fig. 1). Investigation of the same sample convinced us of the absence of appreciable splittings due to coupling with the cadmium isotopes in the ^{1}H NMR spectrum. Coupling between the protons and the mercury nucleus was also not found in the PMR spectrum. The metallic Cd-111 ("Izotop") was provided by L. E. Nivorozhkin.

TABLE 2. Ratios of the Spin–Spin Coupling Constants of the Nuclei of the Metal Atoms $^{199}Hg/^{113}Cd$ with the Corresponding ^{13}C Carbon Nuclei of the Ligand in the Respective Mercury/Cadmium Bisquinoxalylformazanates with Identical Ligands

Ligand	Positions of carbon atoms					
	$c^{(2)}$	$c^{(9)}$	$c^{(10)}$	c^{3}	$c^{1'}$	$c^{1''}$
I	4,273	3,90	?	2,71	5,08	1,83
II	4,03	4,22	2,75	2,86	4,67	1,31
III	3,88	4,00	2,44	2,88	5,09	1,20
IV	4,18	4,22	3,00	2,82	5,40	1,53
V	4,12	?	?	2,73	?	1,40
VI	4,12	4,00	3,43	?	5,20	1,80

TABLE 3. $^{199}Hg/^{113}Cd$ NMR Chemical Shifts in Isostructural Mercury/Cadmium Bisquinoxalylformazanates with Identical Ligands (shifts calculated in parts per million from dimethylmercury and an aqueous solution of cadmium chloride respectively)

Ligand	Hg/Cd shifts
I	-1412,7/140,0
II	-1419,1/127,8
III	-1416,4/120,5
IV	-1443,1/115,9
V	-1436,3/113,2
VI	-1490,9/105,3
VII	—/103.2

In the ^{13}C NMR spectra the satellites from coupling with both isotopes must almost overlap at a working frequency of 50 MHz with $J_{Cd-C} < 40\text{-}50$ Hz and splitting of $(1\text{-}2)\cdot 10^{-8}$. This is supported by experiment (see Fig. 2); the higher sensitivity of the "^{13}C NMR satellites from cadmium" compared with the "^{13}C NMR satellites from mercury" is just as obvious as the substantial advantage in sensitivity for the NMR of cadmium over the NMR of mercury. As a rule the complexes with mercury were less soluble than the complexes with cadmium. The solubilities of the complexes with different ligands also differed by three times. As a rule the solubility was increased by the presence of the alkyl substituents in the structure at 1-Ar and 3-Ar (see the structural schemes of the complexes).

The results of the investigations reported in the present article were based on the data in [6-10]. The ^{13}C and ^{15}N NMR data of the compounds investigated in the present work and of analogous compounds make it possible to establish the coordination point and the size of the metal chelate rings. These results (given in [6-9] for the formazans and formazanates) have also formed the subject of separate publications [10, 11], and some of the data on the ^{13}C NMR of the benzothiazolylformazanates, including the spin–spin coupling constants with cadmium, were published in [12].

EXPERIMENTAL

The ^{13}C, ^{199}Hg, and $^{111,113}Cd$ NMR spectra were recorded on a Bruker CXP-200 spectrometer at the Institute of Heteroorganic Compounds (A. L. Blyumenfel'd). As a rule the preliminary ^{13}C NMR results were obtained on a Varian XL-100 instrument at the Institute of Chemical Reagents and Specially Pure Chemicals (IREA). The ^{13}C NMR spectra of the complexes, dissolved in deuterochloroform at concentrations of 0.01-0.13 mole/liter, were recorded with proton decoupling in tubes with an external diameter of 10 mm as a rule for 10-15 h. In most cases with such long accumulations it was possible to observe the ^{199}Hg and $^{113(111)}Cd$ satellites in the ^{13}C NMR spectra. The ^{199}Hg and $^{113(111)}Cd$ NMR was also as a rule observed in the same tube on the CXP-200 instrument with pulsed proton decoupling and accumulation (4-10 h) at frequencies of about 35 and 44 (44) Hz respectively with accumulations from 600 for cadmium to 16,000 for mercury.

TABLE 4. Spin–Spin Coupling Constants of the Nuclei of the ^{113,111}Cd Metal Atoms with the Corresponding ^{13}C Carbon Nuclei of the Ligand in the Cadmium Bisbenzothiazolylformazanates (Hz) and the ^{113,111}Cd NMR Chemical Shifts in the Same Complexes (ppm from an aqueous solution of cadmium chloride)

Ligand	J_{CdC} with the carbon atoms (Hz)						Shift δ_{Cd}
	$C^{(2)}$	$C^{(9)}$	$C^{(8)}$	C^3	$C^{1'}$ (R^2 = Ar)	$C^{1''}$	
VIII	44	16	13	54	8	18	99,0
IX	42	18	13	49	8	16	97,6
X	47,3 (44,8)	17	14	50	—	16	92,5
XI	46	17	13	44	—	13	90,0
XII	42	17	12	42	—	15	87,7

Of more than 20 lines in the ^{13}C NMR spectra of the cadmium and mercury bisquinoxalylformazanates six of the carbon lines (including the three lines of the heteroaryl carbons) have the satellites (^{113,111}Cd or ^{199}Hg respectively) observed under the conditions described above. They are the lines at δ_C = 152.3-154.9 ($C^{(2)}$ Het), 143-151 ($C^{1''}$, where the lower limit of the range corresponds to the dimethylamine substituent at the *para* position of 1-Ar), 146.5-149.6 (C^3), 138.0-139.1 ($C^{(9)}$ Het), 136.1-138.7 ($C^{(10)}$ Het), and 123-138 ($C^{1'}$, depending on the substituent at the *para* position of 3-Ar from methoxyl to nitro). It is strange, but there is no doubt (from the spectra of the enriched sample) that the carbon line of the heterocycle $C^{(3)}$–Cl at 160-162 does not have observable satellites. As far as the benzothiazolylformazanate complexes are concerned, among the lines having satellites the $C^{1''}$ and $C^{1'}$ signals lie in approximately the same ranges of δ_C (146-151 and about 133 respectively) as in the quinoxalylformazanates. The $C^{(8)}$ Het lines (δ_C = 130.3-130.8) are shifted upfield a little compared with the $C^{(10)}$ lines of the quinoxalylformazanates, and the $C^{(2)}$ Het lines are shifted appreciably downfield (to δ_C = 180-181). We add moreover that if there is an alkyl substituent instead of 3-Ar at the meso-carbon the α-carbon of the alkyl does not have an observable ^3J spin–spin coupling constant with the nucleus of the metal (a shift of the line at 27.9-29.3).

The ^{111}Cd and ^{113}Cd chemical shifts were calculated directly from the line of an aqueous solution of cadmium chloride in a standard sample placed in the same unit (see the spectrum in Fig. 3). The mercury shifts were calculated with reference to dimethylmercury, but in the experiment they were determined by replacing the sample in the unit by a solution of diphenylmercury [the shift of the ^{199}Hg nucleus in $Hg(C_6H_5)_2$ from $Hg(CH_3)_2$ was taken as −791.5 ppm] or by a solution of mercuric chloride in acetone with a ^{199}Hg shift of about −1606 ppm, calculated from dimethylmercury (Fig. 4).

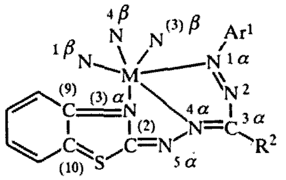
INVESTIGATIONS OF QUINOXALYLFORMAZANATES

The structural formulas of the initial quinoxalylformazans (I-VII) and their complexes (I_M-VII_M) (M = Cd, Hg) are given above. For six (of a total of seven) formazans we had the complexes of both cadmium and mercury. The results from the determination of J_{Hg-C} and J_{Cd-C} from the spectral splitting between the pair of satellites in the cases where they could be observed in the spectrum are given in Table 1. In each column these values are given for two complexes (mercury/cadmium respectively) in the form $|J_{Hg-C}/J_{Cd-C}|$ for the six positions of the carbon in the same ligand. (For the positions of the carbons, see their formulas.) The mercury complex corresponding to the complex (VII_{Cd}) was not obtained. (A dash is used in place of the data for this complex.) The question marks indicate that it was not possible to observe satellites for the given carbon in the spectrum on account of the low signal-to-noise ratio. For convenience of the subsequent discussion Table 2 gives the absolute values of the experimentally obtained numerical ratios of the mercury–carbon constants to the cadmium–carbon constants for the complexes of identical ligands:

$$|J_{Hg,C}/J_{Cd,C}| = |J_{^{199}Hg,^{13}C} : J_{^{113}Cd,^{13}C}|$$

In some cases there no data on one of the values, and a question mark is placed at the corresponding position in the table.

The chemical shifts of the nuclei for the same complexes are given in Table 3. The ^{199}Hg and ^{113,111}Cd NMR chemical shiftswere measuredfor all the indicated complexes of mercury and cadmium. The shifts were measured from an external stand-



M = Hg or Cd
Het = 3-Cl-2-Qnl or (here) 2-Bzt

Fig. 5. Diagram of the coordination polyhedron of the doubly charged d^{10} ion in bis-5-(2-heteroaryl)formazanate. For one of the two ligands coordinating the metal the internal structure giving rise to the presence of π-conjugation in the ligand itself and $d(f)$-π-conjugation in the metal chelate rings is shown.

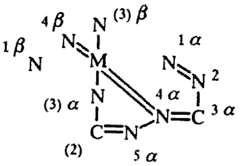


Fig. 6. A simplified diagram of the additional bonds in the coordination polyhedron of mercury bis-5-(2-heteroaryl)formazanate due to f-π-conjugation in the metal chelate rings. The internal structure is shown for one of the two ligands coordinating the metal.

ard (by changing the sample). We point out that according to data in [5] the NMR shift of mercury in $HgCl_2$ in an aqueous solution (at a concentration of 0.5 M) is -1203 ppm from the position of the line for $Hg(CH_3)_2$, which was used as reference in the present work. The mean values of the shifts for the six investigated complexes in scales of the same type can therefore be regarded as 120.5 ppm from cadmium dichloride in water and -233.4 ppm from mercury dichloride also in aqueous solution (see also the data on so-called "absolute" scales of the chemical shift [5, 13]).

INVESTIGATIONS OF BENZOTHIAZOLYLFORMAZANATES

The general structural formula of cadmium 5-benzothiazolylformazanates is given above. (The analogous mercury complexes proved almost insoluble.) The J_{Cd-C} data, obtained from the ^{13}C NMR Cd-satellites of the investigated cadmium 5-benzothiazolylformazanates, are given in Table 4. In one case for compound (X) only the satellites from ^{111}Cd and ^{113}Cd were partially separated in the spectra (see Table 4).

It is, of course, necessary to consider the comparative values of the spin–spin coupling constants of the cadmium nuclei with the carbons and the free observation of these constants for the benzothiazolylformazanates in conjunction with the same data for the quinoxalylformazanates, since here there are no fundamental differences between the two types of complexes. First, the fact that $J_{Cd,C}$ is observed (which is not in itself always possible) is important, since the complexes and organometallic compounds of cadmium are extremely susceptible to metallotropic transformations and sometimes even at room temperature. The observation of the spin–spin coupling constants demonstrates the considerable stability of the complexes studied in the present work. Second, the largest values are obtained for the spin–spin coupling constants with the carbons included in the metal chelate rings, i.e., with the meso-carbon of the formazan chain C^3 (in the order of 50 Hz) and with the *ipso*-carbon of

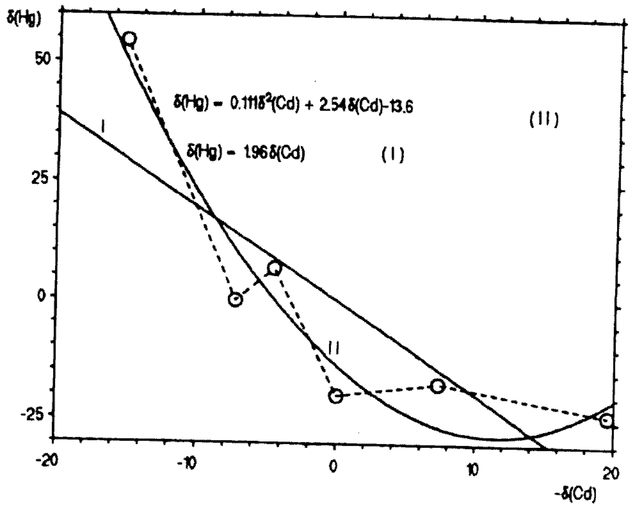


Fig. 7. A graphical representation of the functional relationship between the chemical shifts of the cadmium and mercury nuclei in bisheteroarylformazanate complexes with identical ligands. The shifts are calculated from the corresponding mean values for the six pairs of isostructural complexes (cadmium and mercury respectively) with the formazans (I-VI) presented here. The experimental points are represented by the circles linked by a dotted line, and the linear and quadratic approximations are given.

the heteroaryl added to the N^5 atom of the formazan (in the order of 35-45 Hz) and are appreciably larger for benzothiazolyl than for quinoxalyl. The other carbons having appreciable (measurable) spin–spin coupling constants are closest to the nitrogen atoms coordinating the metal (the "coordination points") or belong to the heterocycle, i.e., are included as it were in the parallel "main" (i.e., metal chelate) chain of conjugation. The *ipso*-carbon of 3-Ar has an appreciably smaller spin–spin coupling constant with the cadmium nucleus than the analogous carbon of 1-Ar, although their positions in relation to the metal chelate ring are analogous. On the other hand this advantage of 1-Ar is absent for the spin–spin coupling constant with mercury, and the opposite situation arises. This once again demonstrates the specific differences between the 4*d* element Cd and the 5*d*,4*f* element Hg in the mechanisms of transmission of spin–spin coupling from the nucleus of the metal to the nuclei of the ligand. We will attempt to discuss these differences below. To conclude the preliminary discussion, which was essential during presentation of the data, we point out that by virtue of the procedure available to us the measurements of J were conducted with an accuracy up to the sign, i.e., it is tacitly assumed that the signs of J_{Hg-C} and J_{Cd-C} are opposite, since the gyromagnetic ratios of mercury and cadmium have different signs. However, it cannot be ruled out that the situation may be different for some positions of C.

As was demonstrated back in [1, 2] and then in a series of x-ray crystallographic and NMR investigations [12, 14, 15] (see also ^{15}N NMR in [11]), the structure of the biscomplexes of the 5-(2-heteroaryl)formazanates investigated in the present work is pseudooctahedral both in the crystal and in solution, as shown diagrammatically in Fig. 5.

The doubly charged ions of the zinc group, to which Cd^{2+} and Hg^{2+} belong, have completely filled highest *d*-shells (4*d* and 5*d* respectively), and Hg^{2+} also has a completely filled 4*f* shell. The relationships governing the formation of molecular orbitals containing both the orbitals of the central ion and linear combinations of the orbitals of the coordination points were discussed in [16] (see pp. 110-111).

According to the accepted standards [16], for an octahedral environment the atoms of the ligand coordinating the metal are numbered from 1 to 6. In the system of coordinates related to the metal the 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, for the strictly octahedral 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). Such a complex can be used as a model.

The considerations that hold rigorously for an ideal coordination octahedron are roughly approximations for a highly distorted octahedron (of the trigonal antiprism type [17-19]). The real structure of the coordination octahedron, proved for the investigated compounds or their analogs, must be taken as a distortion, which is not however fundamental from the qualitative standpoint. It is clear that approximately unit charge is transferred from the M^{2+} ion to the N^1 atoms of each of the two ligands. Furthermore, there is no doubt that an almost fully symmetrical MO with a linear combination of the σ orbitals of all six coordination points is also formed by the six σ orbitals of the central ion. The antisymmetric MOs form π bonds with the π orbitals of each pair of coordination points of the different ligands arranged symmetrically in relation to the metal. The formation of these MOs (to a first approximation, of course) does not lead to any difference in the electronic structure of each of the coordination points.

The MOs fully symmetrical with respect to all the π orbitals of the coordination points are formed with the participation of three d_ε orbitals. The overall MO of such a type is in fact fully symmetrical in relation to any permutations of the coordination points.

The formation of MOs with the participation of the d_ε orbitals of the metal undoubtedly leads to a reduction of symmetry. In this case it is logical to expect tetrahedral distortion, i.e., the appearance of an isolated axis, which is most likely directed along the line linking the metal to the coordination point, where the electronic density is minimal: $N^{4\alpha}-M-N^{4\beta}$. (In this case, as in Fig. 5, the superscripts α and β refer to the different ligands.)

Another argument was put forward in relation to the complexes of mercury compared with the complexes of cadmium. For the *f* orbitals of a metal the MOs forming the "π bonds" have one of two different types of symmetry. In [16] it was suggested that the MOs must be arranged in order of increase in energy in such a way that the *f* orbitals form the highest MOs (antibonding MOs with the participation of the *f* orbitals of the metal). Whereas such groups of orbitals are indeed unimportant for the energetics and the geometric structure of the complex, they can play a large part in the magnetic properties of the complex, such as the transmission of spin–spin coupling. For us it is important that the overall MO is no longer symmetric (and is not antisymmetric) with reference to the coordination points even for an octahedral environment. This situation is shown provisionally in Fig. 6. One pair of points (if the possible differences in the coefficients at the respective orbitals for various values of k are ignored) does not give any contribution at all to such an overall orbital. (The contributions from MOs with different symmetry are compensated on account of the difference in the signs before the respective orbitals — these are the contributions from the third and sixth points.) For the other pair such compensation will be partial (points 2 and 5, for which only one each of the contributions π_x and π_y is compensated for each coordination point). For the third (points 1 and 4) there is no compensation — there is as it were a double additional bond. To conclude the discussion of the octahedral model we once again recall that the numbering of the coordination points here corresponds to the arbitrary numbering in [16] but in no way corresponds to the numbering of the coordination points in Figs. 5 and 6 and in the other structural schemes and tables. It can only be supposed that N^4, for example, would correspond to point 1, $N^{(3)}$ (belonging to the heteroaryl) would correspond to point 2, and N^1 would correspond to point 3. The effects of the *f* orbitals for the given model in terms of group theory will be examined in greater detail in future publications.

The x-ray crystallographic data indicate the presence of π conjugation (the planarity of the ligand in the complex, the alternation of the bond lengths, etc.). On the basis of these facts and of the discussion of the model complex above it is possible to explain the ratio of the spin–spin coupling constants of mercury and cadmium if only semiquantitatively. The simplified but qualitatively almost irreproachable ideology, which makes it possible to determine the values of the spin–spin coupling constants, corresponds to the model of the spin–spin coupling constant adopted by Pople and Santry [20, 21]. Since the value of the spin–spin coupling constant between nuclei *a* and *b* is equal to $J_{ab} \propto \gamma_a \gamma_b \langle H_{ij} \rangle^2$, where γ is the gyromagnetic ratio of the nuclei and $\langle H_{ij} \rangle^2$ is the square of the matrix element of the perturbation in the first order (*i* is the ground and *j* is the excited level), and $\langle H_{ij} \rangle^2 \propto (1/\Delta E_{ij})^2 \propto n^2$, where *n* in turn is the principal quantum number of the atomic orbital forming the MO. The approach is obviously simplified (if only in the fact that the sum with respect to the various *j* values was omitted not to mention the fact that the difference in the energies of the AOs was used instead of the MOs). Nevertheless, for the ratio of the spin–spin coupling constants of the mercury and cadmium nuclei in the simplest dialkylmetals $M(CH_3)_2$ and $M(CH_2CH_3)_2$ calculation in the form indicated above gives:

$$| J_{Hg-C} / J_{Cd-C} | = | (\gamma_{199Hg} / \gamma_{113Cd}) | \cdot (5/4)^2 \cong 0{,}804 \cdot 1{,}563 \cong 1{,}257$$

and the respective ratios $|{}^1J_{Hg,C}/{}^1J_{CD,C}|$ are in fact equal to 1.281 for the dimethyl compounds [22-24] and 1.248 for the diethyl compounds [22, 25] (see also [26]). Comparing this result with the data in Table 2, it is impossible not to see two obvious contradictions. The first lies in the values that for the $|J_{Hg,C}/J_{Cd,C}|$ values obtained in the present work can exceed this result by three times. This may indicate a role for conjugation in the metal chelate rings in the transmission of spin–spin coupling. Second, the $|J_{Hg,C}/J_{Cd,C}|$ values for the various carbons differ by 3-4 times. The only qualitative explanation for this fact is the presence in the mercury of additional and moreover nonequivalent (for the various coordination points) "bond channels," i.e., additional MOs including the orbitals both of the metal and of the ligand atoms. What these "additional channels" may be and how they may differ for the various coordination points we have already discussed in terms of the simplified model according to [16].

The other data on the spin–spin coupling constants, given in Tables 1, 2, and 3, do not probably require further discussion. It is sufficient merely to mention the role of π-conjugation between the system of carbon and nitrogen atoms of the metal chelate ring and the orbitals of the metal and the conjugation between the azaheteroaryl and the metal chelate rings of the complex during the transition to the imino form.

The ^{113}Cd and ^{199}Hg chemical shifts in the complexes, measured from the shifts of MCl_2 in aqueous solution, amount to about 10% of the above-mentioned full scales (about 120 ppm of 1106 ppm for cadmium and about −233 ppm of 2432 ppm for mercury). However, the signs of these shifts in relation to the relevant standards do not coincide, which is hardly surprising. Attempts to compile scales of chemical shifts for the isotopes of the elements of one group, belonging to different periods, almost always lead to failure (e.g., see [27], where the scales of ^{29}Si and ^{13}C shifts are compared). The effects of the substituents at the *para* positions of 1-Ar and 3-Ar for the mercury shifts compared with cadmium coincide in sign (which is clear from the relation presented in Fig. 7) and are approximated fairly well by the quadratic dependence of $\Delta\delta_{Hg}$ on $\Delta\delta_{Cd}$, where $\Delta\delta$ corresponds to the increment to the shifts due to the respective substituents at the *para* positions of 1-Ar and 3-Ar (a set of two substituents):

$$\Delta\delta_{Hg} \cong 0{,}111(\Delta\delta_{Cd})^2 + 2{,}54\,\Delta\delta_{Cd} + 13{,}3$$

or by the rough linear approximation:

$$\Delta\delta_{Hg} \cong 1{,}96\,\Delta\delta_{Cd},$$

which also corresponds approximately to the ratio of the shifts, proportional to the ratio of the "absolute" scales.

We would also like to draw attention to the fact that the appearance of conjugation effects in metal chelate rings was first observed by ourselves in conjunction with Yu. S. Ryabokobylko for 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 [1, 28].

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