

Structure and Stability of Complexes of *N,N'*-Di(9-anthrylmethyl)-1,2-diaminoethane with Cations of Metals from IIB group: Quantum-chemical Study

T.N. Gribanova¹, A.D. Dubonosov², I.E. Tolpygin², V.P. Rybalkin¹,
V.A. Bren'¹, R.M. Minyaev¹, and V.I. Minkin¹

¹Research Institute of Physical and Organic Chemistry at Rostov State University, Rostov-on-Don, 344090 Russia
e-mail: dubon@ipoc.rsu.ru

²Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, 344090 Russia
e-mail: ssc-ras@mmbi.krinc.ru

Received November 12, 2004

Abstract—Structural and energy characteristics of *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane complexes with Zn²⁺, Cd²⁺, and Hg²⁺ cations were investigated applying the method DFT (B3LYP/LanL2DZ). The interaction of the diamine with the metal cations results in formation of complexes with various types of structures containing a di-, tri-, or tetracoordinated metal, the latter complexes being the most stable. In all types of complexes the energy of complexing decreases in the series Zn²⁺, Hg²⁺, Cd²⁺ and is determined by combined effect of steric and orbital factors.

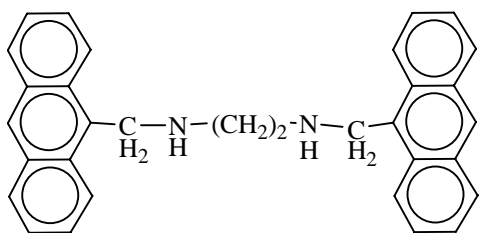
One of priorities of the modern chemistry is a development of efficient methods for environmental control based on the chemical analysis of the objects constituting the environment. In this connection the studies directed to the search for highly sensitive chemosensor systems making it possible to determine the content of various elements in the biological systems acquire a vital importance. [1]. The experimental investigation of chemosensors is extensively carried out nowadays, and it has revealed quite a number of versatile sensor systems [1, 2], but the nature of their selectivity is not necessarily unambiguously understandable within the framework of the experimental approach. Systematical theoretic investigations of chemosensor systems are not yet widespread. However the detailed study of factors governing the action of various sensors within the framework of quantum-chemical analysis may provide additional opportunities for the search and purposeful modeling of new sensor systems.

Promising candidates for the role of new highly sensitive chemosensors are derivatives of *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane (**I**) formerly studied by means of IR and NMR spectroscopy [3]. As shown by the experimental investigation of reaction between compound **I** and cations of the IIB group diamine **I** possesses enhanced sensitivity toward zinc cations and can be

recommended as potential sensor. At the same time, practically no data were published both on the structure of the arising complexes and on the factors governing the selectivity of these interactions.

This study is aimed at elucidation of the selectivity nature of diamine **I** by quantum-chemical methods. Applying calculations by procedures of density functional theory DFT (B3LYP/LanL2DZ) [4, 5] we investigated energy and geometrical characteristics of initial diamine **I** and its complexes with cations of the IIB group metals (Zn²⁺, Cd²⁺, Hg²⁺), performed an analysis of the relative stability of the corresponding structural isomers, and studied the factors determining the complexing efficiency in these systems.

The calculations were performed by the method of density functional theory (DFT) using a three-parameter potential B3LYP in a pseudopotential basis LanL2DZ [4, 5] applying a software package [5] Gaussian-98. The stationary points on the potential energy surface (PES) were identified by means of analytical calculation of the second derivatives matrix (force constants). The graphical images of the molecular structures shown on the figures were obtained applying the program PD (PLUTO mode) in the framework of the software package PC MODEL [6] using as input parameters the final Cartesian



I

coordinates of the atoms obtained by geometry optimization.

Structure of *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane. The calculations demonstrate that *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane can exist in the form of a series of conformers corresponding to the energy minima ($\lambda = 0$, here and hereinafter λ denotes the number of negative eigenvalues of Hesse matrix in a given stationary point) on PES. The energy dif-

ference between various conformers is no more than 3 kcal mol⁻¹, and their structural characteristics are also very similar. The structures of the most characteristic conformers of *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane are presented on Fig. 1, their energy parameters are given in Table 1.

According to calculations conformers **I–III** with the *cis*-position of nitrogen centers may interact with cations Zn²⁺, Cd²⁺, and Hg²⁺ providing complexes of various structural types. In all cases the metal interacts simultaneously with the two nitrogen sites of the diamine. With *trans*-conformer **IV** the stereochemical conditions prevent the interaction of cation with both nitrogen atoms, and the attractive interaction between the metal and the diamine does not take place: The optimization of the corresponding structure results in decomposition of the associate into the initial components. The interaction of

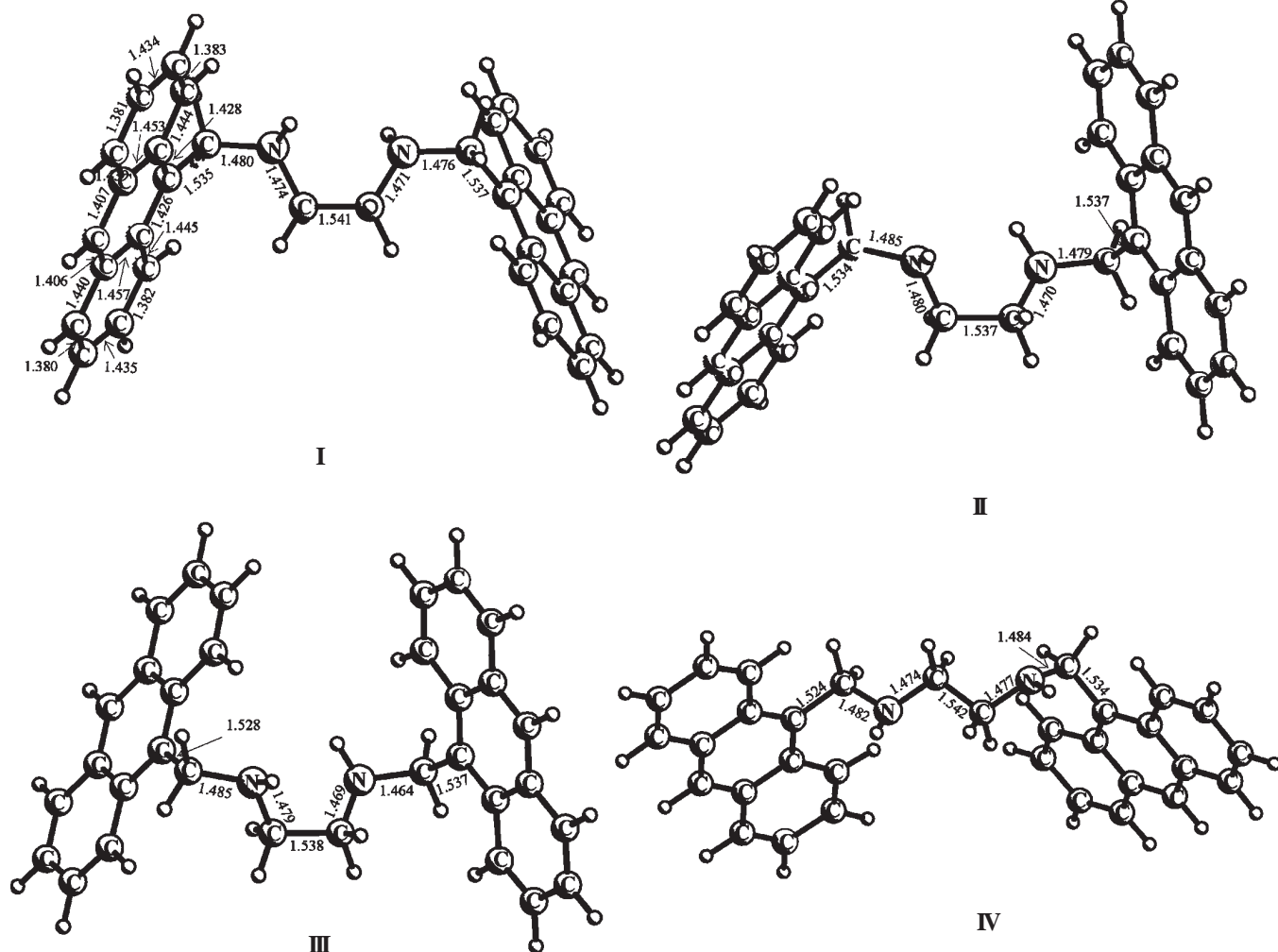


Fig. 1. Geometrical characteristics of conformers **I–IV** calculated by the method DFT (B3LYP/LanL2DZ). Here and hereinafter on all figures the bond lengths are given in angstroms, and the angles in degrees.

Table 1. Energy parameters^a calculated by the method DFT (B3LYP/LanL2DZ) for conformers **I–IV** and complexes **V–VII** corresponding to energy minima ($\omega = 0$) on PES

Structure no.	E_{total}	ZPE	ΔE	E_{complex}	ω_1
I	–1345.565685	0.521913	2.90	–	2.5
II	–1345.570311	0.522643	0	–	9.7
III	–1345.569010	0.522289	0.82	–	11.9
IV	–1345.566816	0.521806	2.19	–	5.1
Va	–1410.650280	0.525861	32.39	287.58	9.2
Vb	–1393.119298	0.525280	26.47	249.59	10.6
Vc	–1387.796284	0.524561	9.63	274.30	9.8
VIa	–1410.688260	0.526641	8.56	308.51	12.4
VIb	–1393.142859	0.525952	11.69	261.47	11.8
VIc	–1387.802131	0.525515	5.96	275.07	9.9
VIIa	–1410.701896	0.527004	0	317.88	15.1
VIIb	–1393.161485	0.526319	0	273.97	13.7
VIIc	–1387.811630	0.525878	0	281.84	13.2

^a \hat{A}_{total} is total energy (a.u. where 1 a.u. = 627.5095 kcal mol^{–1}); ZPE is the energy of zero harmonic oscillations (a.u.); ΔE is a relative energy (kcal mol^{–1}); E_{complex} is energy of complex formation (kcal mol^{–1}); ω_1 is the smallest harmonic frequency (cm^{–1}).

the *cis*-conformers of the diamine with cations Zn²⁺, Cd²⁺, and Hg²⁺ affords complexes **V**, **VI**, and **VII** formed from conformers **I**, **II**, and **III** respectively. The arising complexes are distinguished by the configurations of the metal center bonds: in complexes **V** the metal is bicoordinated and interacts only with the nitrogen atoms; in complexes **VI** the metal center interaction alongside that with the nitrogen centers occurs also with the π -system of one of the anthracene substituents, and thus the metal is tricoordinated; complexes **VII** are characterized by tetracoordination of the metal which interacts at once with two anthracene substituents and two nitrogen centers. The calculations showed that for all cations in question the thermodynamic stability of the complexes grew in going from **V** to **VI** and further to **VII**.

Structure and stability of complexes **V**.

In a complex series **V–VII** complexes **V** are the least stable, possess C_{2v} -symmetry, and contain a bicoordinated metal interacting with two nitrogen sites of the diamine. The energies of complexes **V** stabilization calculated as the difference between the total energy of the complex and the sum of energies of the corresponding diamine conformer and metal cation decrease in the series Zn²⁺, Hg²⁺, Cd²⁺ and amount respectively to 287.6, 274.3, and 249.6 kcal mol^{–1}. The geometrical parameters of complexes **V** are presented on Fig. 2, and their energy characteristics are given in Table 1.

In the series of complexes **V** zinc complex **Va** possesses the largest energy of complex formation. The

reaction of zinc cation with diamine in complex **Va** results in formation of two Zn–N bonds whose length (2.149 Å) is within the known range [7] of coordination Zn–N bonds. The buildup of the complex is accompanied by a notable weakening of the bonding of the nitrogen atoms with the other substituents and by expansion of the coordination unit HN(CH₂)₂NH compared with the initial diamine.

The increase in the cation radius in going from zinc to cadmium complex **Vb** impairs the stereochemical conditions of interaction M–N in a five-center coordination unit resulting in a considerable reduction of the bond angle NCdN (79.8°) compared with the analogous zinc complex (88.6°). The interatomic distances Cd–N in **Vb** are 2.407 Å. The formation of complex **Vb** is characterized by less pronounced than in zinc case changes in the structural characteristics of the initial diamine evidencing the weakening interaction between the metal and nitrogen centers in the cadmium complex. The calculated energy of complex formation with cadmium is by 38 kcal mol^{–1} less than for the zinc complex.

Mercury complex **Vc** like the above considered complexes is stabilized by interaction of the metal with the nitrogen centers resulting in two coordination bonds Hg–N (2.673 Å). The formation of Hg–N bonds is accompanied by lengthening of the bonds between the nitrogens and other substituents as compared with the initial diamine, but these changes are less pronounced than in complexes **Va** and **Vb**. In the series of metals

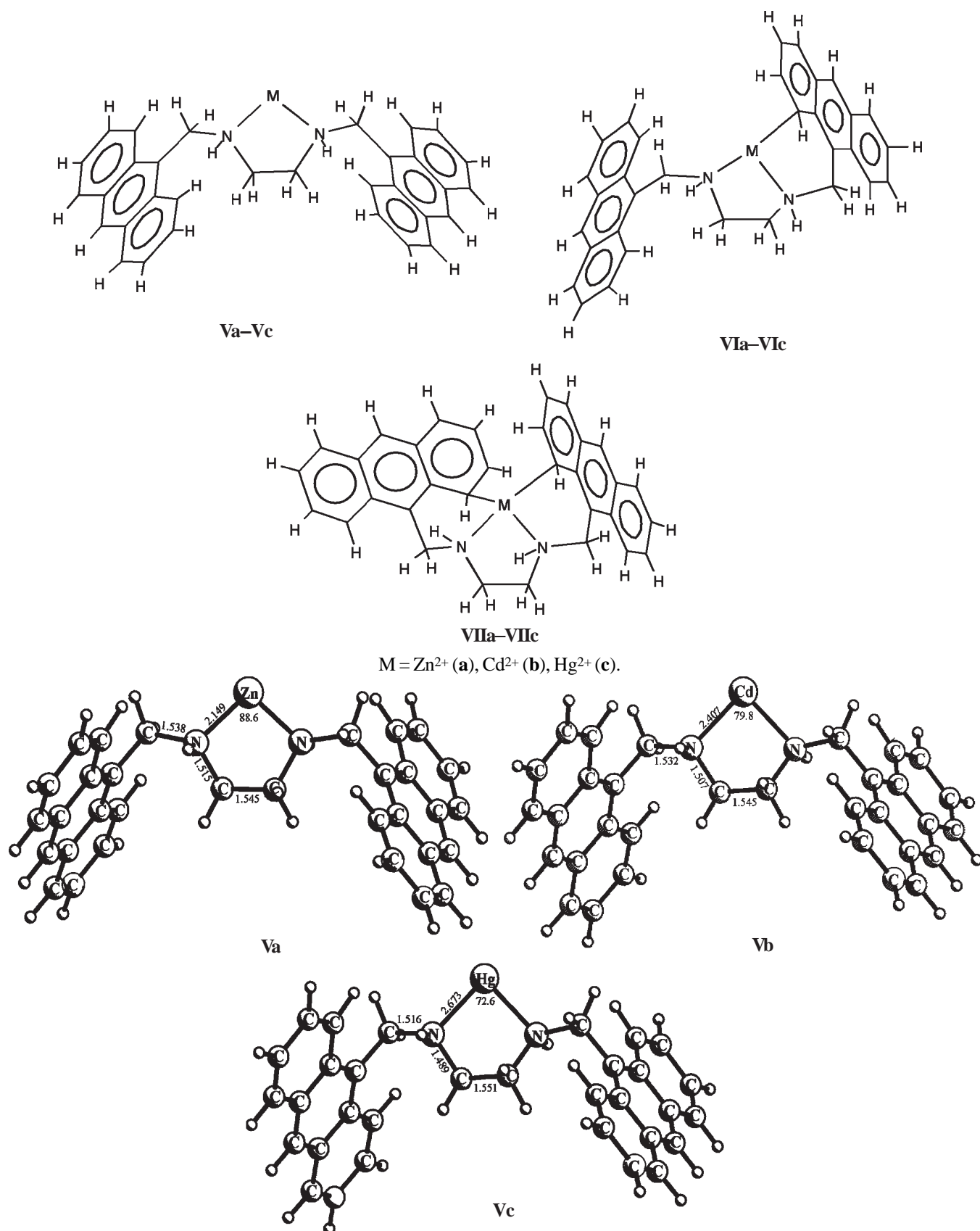


Fig. 2. Geometrical characteristics of complexes V calculated by the method DFT (B3LYP/LanL2DZ).

under study the mercury has the largest cation thus creating the most strained steric conditions for interaction in the five-center coordination unit $\text{NHgN}(\text{CH}_2)_2$ resulting in further decrease in the angle NMN in the complex (NHgN 72.7°). However the calculated energy of stabilization of complex **Vc** proved to be by $\sim 25 \text{ kcal mol}^{-1}$ larger than that of the cadmium complex.

Structure and stability of complexes VI. In complexes **VI** the metal is tricoordinated and interacts apart the nitrogen centers with a π -system of one of

anthracene substituents. The additional interaction increases the stability of complexes **VI** compared with complexes **V**. As in the complexes **V** the energy of complex formation of complexes **VI** decreases in the series Zn^{2+} , Hg^{2+} , Cd^{2+} and equals respectively to 308.5, 275.1, and 261.5 kcal mol^{-1} . The geometrical parameters of complexes **VI** are presented on Fig. 3, and their energy characteristics are given in Table 1.

The most significant stabilization due to the additional attractive interaction of the metal with the anthracene

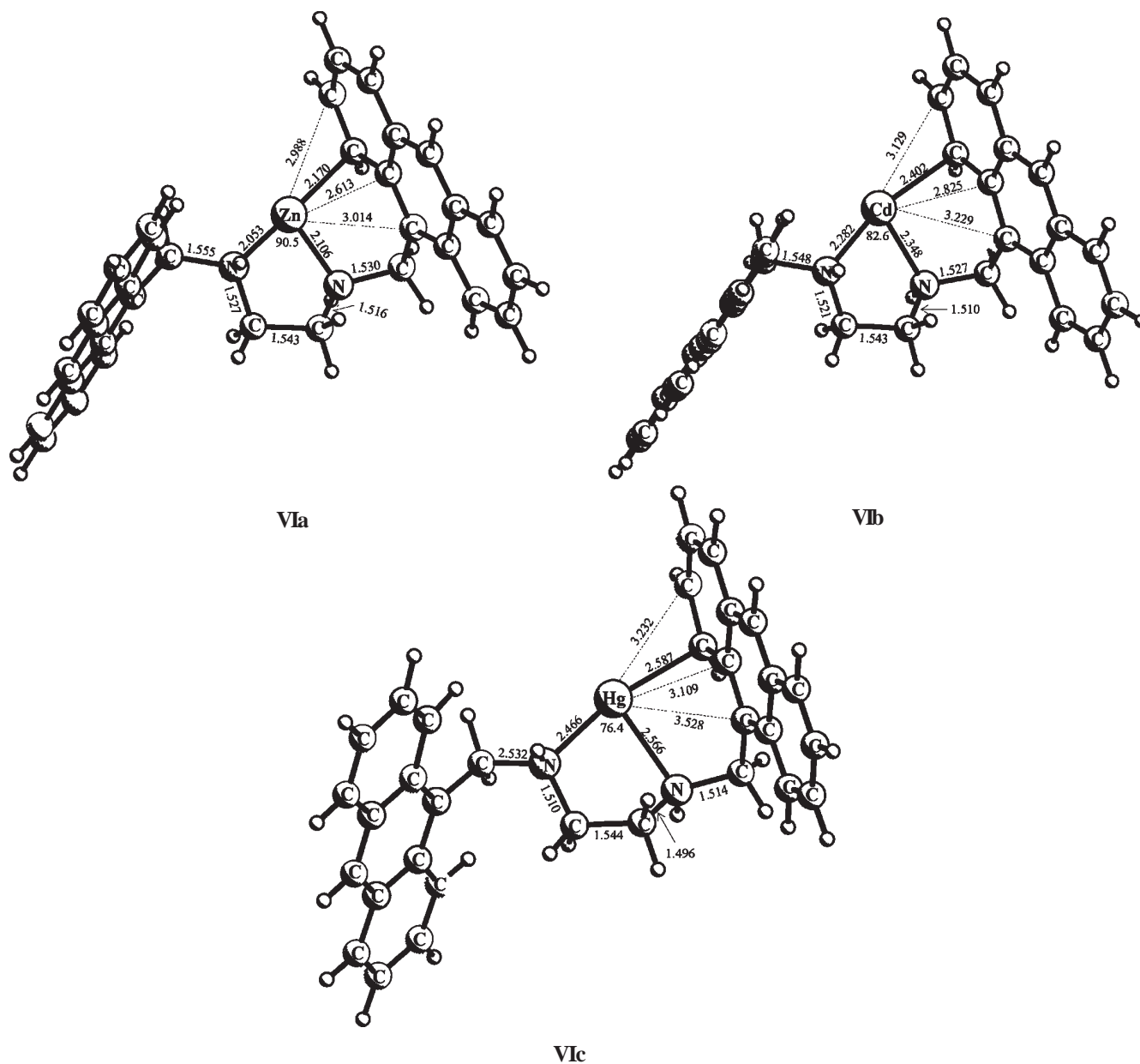


Fig. 3. Geometrical characteristics of complexes **VI** calculated by the method DFT (B3LYP/LanL2DZ).

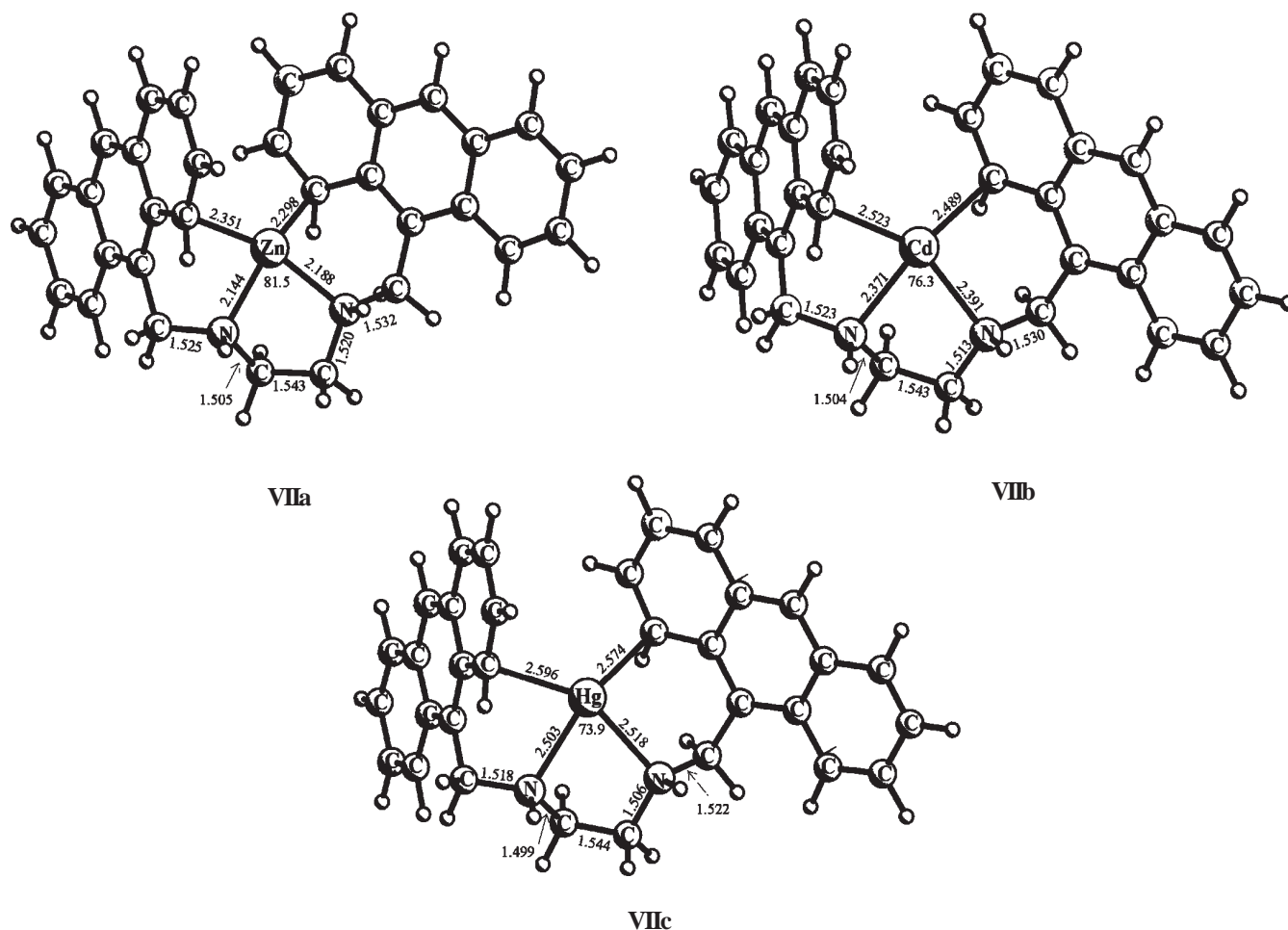


Fig. 4. Geometrical characteristics of complexes **VII** calculated by the method DFT (B3LYP/LanL2DZ).

fragment is observed in zinc complex **VIa** where the energy of complex formation exceeds that of complex **Va** by ~ 21 kcal mol $^{-1}$. In complex **VIa** a strongly flattened T-like configuration of the tricoordinated metal center is formed with two nonequivalent Zn–N bonds and a Zn–C bond 2.170 Å long. The other revealed interactions Zn–C are characterized by far longer contacts (Fig. 3). The additional coordination results in the strengthening zinc bonds with the nitrogen centers and in shortening Zn–N bonds compared to complex **Va**. The other structural manifestation of the attractive interaction between zinc and the anthracene substituent is the pronounced distortion of the planarity of the anthracene moiety: The hydrogen atom attached to the carbon involved into the shortest Zn–C contact is displaced out of plane to $\sim 26^\circ$, whereas the distortion of the planarity of the carbon skeleton is less significant and does not exceed 5° .

In going to cadmium complex **VIb** the decrease in its stability compared to zinc complex **VIa** is even more

pronounced than in the case of complexes **V** and amounts to ~ 47 kcal mol $^{-1}$. In complex **VIb** the configuration of bonds of the tricoordinated cadmium center is far less flattened than in complex **VIa**. The additional coordination in complex **VIb** is accompanied with notable shortening of the Cd–N bonds compared to complex **Vb**; however the thermodynamic feasibility of complex **VIb** with respect to **Vb** is less pronounced than in zinc complexes, and amounts to 11.9 kcal mol $^{-1}$ indicating weakening of the metal interaction with the π -system of anthracene in going from zinc to cadmium.

The energy of stabilization of mercury complex **VIc** like in the case of complexes **V** is intermediate in the series of complexes **VI**, but the decrease in the energy of complex formation in going from Zn to Hg is more pronounced than in the series of complexes **V** (33.4 and 13.3 kcal mol $^{-1}$ respectively). Although the interaction of the mercury with the anthracene moiety in complex **VIc** results in the strengthening of Hg–N bonds, the energy

of complex formation compared to complex **Vc** increases only by 0.8 kcal mol⁻¹ and thus the efficiency of the additional coordination is negligible in the case of mercury.

Structure and stability of complexes **VII**.

Complexes **VII** are characterized by the presence of tetracoordinated metal interacting with nitrogen centers and two anthracene moieties. In the series of complexes **V–VII** the highest energies of formations correspond to complexes **VII**. In the same way as with the other complexes the energies of formation of complexes **VII** decrease in the series Zn²⁺, Hg²⁺, Cd²⁺ and amount to 317.9, 281.8, and 274.0 kcal mol⁻¹ respectively. The geometrical parameters of complexes **VII** are presented on Fig. 4, and their energy characteristics are given in Table 1.

The configuration of the coordination center in complexes **VII** is a distorted tetrahedron with two pairs of nonequivalent bonds (Fig. 4). The building up of a tetrahedral structure including two bulky anthracene ligands imposes more stringent spatial requirements and brings on weakening of the metal–ligand bonds in complexes **VII** as compared with those in complexes **V** and **VI**. At the same time the interaction of the metal with the second anthracene substituent is thermodynamically favorable and results in even more pronounced than in complexes **VI** stabilization of complexes **VII** as compared to that of **V**.

Like the metal bonding to a single anthracene fragment, the interaction of a metal with two anthracene substituents is the most efficient in the case of zinc where the transition of the metal from the bicoordinated to tetracoordinated state results in increase in the energy of complex formation by 30.3 kcal mol⁻¹. The efficiency of the additional π -interaction is lower in the case of cadmium complexes (the increase in the energy of complex formation by 24.4 kcal mol⁻¹), and the formation of the tetrahedral configuration of the metal center was the least feasible for mercury complexes: The thermodynamic stability of complex **VIIc** exceeds that of **Vc** only by 7.5 kcal mol⁻¹. In going from complexes **V** to complexes **VI** and further to complexes **VII** the preferable interaction of diamine with zinc as compared to cadmium and mercury becomes more pronounced.

Hence systems **VII** are preferred products of complex formation of *N,N'*-dianthryl-1,2-diaminoethane with metal IIB group cations, and the maximum efficiency of the interaction is characteristic of zinc.

Effect of steric and orbital factors on formation of complexes **V–VII.** The efficiency of the interaction

between a sensor and a substrate is regulated by the factors of steric and electronic concordance [1] where the effects of orbital interactions may be of major importance. The stabilization of complexes **V–VII** according to the calculations is provided by formation of two types of interaction between the components: The metal interacts with the nitrogen centers and the π -system of the anthracene substituents. The effect of the steric and electronic factors of the metal–nitrogen bonding may be conveniently analyzed by an example of complexes **V** stabilized by attractive interactions only of this type.

The data of NBO-analysis show [8] that the main attractive component in formation of complexes **V** consists in donation of the electron density from the unshared electron pairs of nitrogen to the unoccupied *s*-orbital of the metal [$n_N \rightarrow s^*(M^{2+})$]. The efficiency of this interaction is governed essentially by the size of the energy gap between the interacting orbitals and by diffuseness of the metal *s*-orbital. The molecular-orbital analysis indicates that in the series Zn²⁺, Cd²⁺, Hg²⁺ the energy of the *s*-orbital decreases and the energy gap diminishes. This circumstance ensures potentially the best conditions of orbital interaction for the mercury and the worst for zinc. On the contrary, the growing cation radius in going from zinc to cadmium and further to mercury causes the increase in steric strain in the five-centered coordination structure enhancing the effect of the steric destabilization of the complex in the series Zn²⁺, Cd²⁺, Hg²⁺. Thus the changes in steric and orbital interactions in the series Zn²⁺, Cd²⁺, Hg²⁺ possess the opposite trends providing a possibility to understand the non-monotone variation of the energy of complex formation in this series. The notable

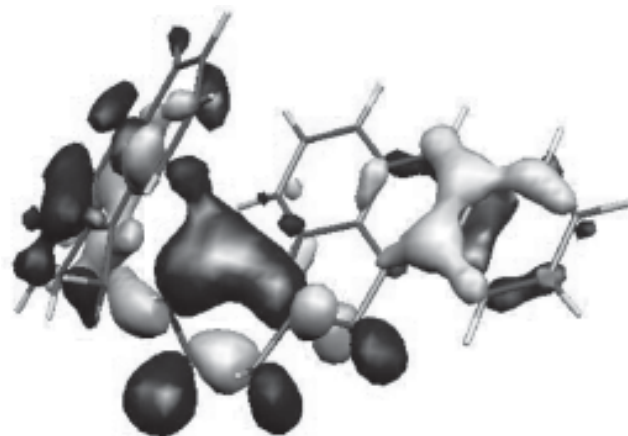


Fig. 5. The form of a bonding molecular orbital *a* corresponding to the orbital interactions of fragments in complex **VIIa**.

Table 2. Energies of orbital interactions (kcal mol⁻¹) between diamine and metal cation M²⁺ in complexes **VII** calculated by NBO scheme

Compd. no.	$E[n_N \rightarrow s^*(M^{2+})]$	$E[p_{ant} \rightarrow s^*(M^{2+})]$	$E[s^*(M^{2+}) \rightarrow p_{ant}^*]$
VIIa	45.88	43.30	99.34
VIIb	37.56	35.74	13.48
VIIc	42.34	54.67	10.77

preference of complexing with zinc is ensured not only by favorable steric conditions but also by greater diffuseness of the zinc orbitals enhancing the efficiency of the orbital interactions. At the same time the worse stereochemical conditions in the case of mercury impair the optimum orientation of the unshared electron pairs of the nitrogen thus weakening the efficiency of the orbital interaction.

In complexes **VI** and **VII** alongside the stabilization effects from donation of the electron density of the unshared electron pairs of the nitrogen to the metal *s*-orbital [$n_N \rightarrow s^*(M^{2+})$] the interaction of the metal with the anthracene moieties also contributes to the energy of complex formation. As revealed the NBO-analysis of the most stable complexes **VII** the energies of interaction [$n_N \rightarrow s^*(M^{2+})$] diminish in the series Zn²⁺, Hg²⁺, Cd²⁺ (Table 2) and correlate with the trend in variation of the energy of complex formation. The interaction of the metal *s*-orbital with the orbitals of the unshared electron pairs of the nitrogen is well illustrated by the view of molecular orbital *a* shown on Fig. 5.

The main attractive component in the interaction between the metal and anthracene substituents according to the NBO-analysis consists in donation of the electron density from the occupied bonding δ -orbitals of anthracene to the unoccupied *s*-orbital of the metal [$\pi_{ant} \rightarrow s^*(M^{2+})$]. At the same time according to the calculations the electron density accepted by the metal *s*-orbital can be involved into the process of the back donation to the antibonding π -orbitals of the anthracene rings [$s^*(M^{2+}) \rightarrow \pi_{ant}^*$] also significantly contributing to the energy of complex formation. The energy of electron density donation $s^*(M^{2+}) \rightarrow \pi_{ant}^*$ is determined by the approach of the interacting orbitals and is especially large for zinc (Table 2) ensuring the high efficiency of its interaction with diamine. For cadmium and mercury the efficiency of the back donation is small.

Therefore the calculations performed show that alongside the coordination “metal–nitrogen” the interaction

between the metal and anthracene substituents considerably contributes to the stabilization of complexes of *N,N'*-di(9-anthrylmethyl)-1,2-diaminoethane with metal cations of the IIB group. The theoretical results confirm the experimental conclusion on preferable complexing of diamine **I** with zinc cations as compared to cadmium and mercury due to combined effect of factors of steric and orbital concordance.

The study was financially supported by grants CRDF/Ministry of Education of the Russian Federation (RO-004-X1), BRHE 2003 Post-Doctoral Fellowship (Y1-C-04-03), The Program of President supporting the scientific schools (project NSh no. 945.2003.3), Russian Foundation for Basic Research (no. 05-03-32470), and Program of Fundamental Research of Russian Academy of Sciences “Development of Technology of Monitoring, Ecosystems Simulation and Prediction in the Study of Natural Resources under Conditions of Arid Climate”.

REFERENCES

- Bren', V.A., *Usp. Khim.*, 2001, vol. 70, p. 1152.
- Bourson, J., Badaoui, F., and Valeur, B., *J. Fluoresc.*, 1994, vol. 4, p. 275; Valeur, B. and Leray, I., *Coord. Chem. Rev.*, 2000, vol. 205, p. 3; Prodi, L., Boletta, F., Montali, M., and Zaccheroni, N., *Coord. Chem. Rev.*, 2000, vol. 205, p. 59.
- Tolpygin, I.E., Bren', V.A., Dubonosov, A.D., Minkin, V.I., and Rybalkin, V.P., *Zh. Org. Khim.*, 2003, vol. 39, p. 1435.
- Foresman, J.B. and Frisch, E., *Exploring Chemistry with Electronic Structure Methods*, Pittsburg: Gaussian, Inc., 1996, 302 p.
- Gaussian 98, Revision A.9*, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A.Jr., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., Pople, J.A. Pittsburgh, PA: Gaussian, Inc., 1998.
- PCMODEL, Selena Software*, Bloomington, 1987.
- Wells, A. F., *Structural Inorganic Chemistry*, Oxford: Clarendon, 1984, 5 ed.
- Reed, A.E., Curtiss, Z.A., and Weinhold, F., *Chem. Rev.*, 1988, vol. 88, p. 899.