

# Quantum-Chemical Calculations of (5.6.5) Macrotricyclic Complexes in Some $M^{II}$ – (N,S)–Ambidentate Ligson – (O)–Ligson Triple Systems

Denis V. Chachkov<sup>b</sup> and Oleg V. Mikhailov<sup>a@</sup>

<sup>a</sup>Kazan State Technological University, 420015 Kazan, Russia

<sup>b</sup>Super-Computer Center of KSC RAS, 420008 Kazan, Russia

@Corresponding author E-mail: ovm@kstu.ru

*The data of quantum-chemical calculations of structures of (5.6.5) macrotricyclic metallocomplexes that may be formed as a result of template synthesis in the  $M^{II}$  – organic compounds having N and S donor atoms [(N,S)-ligson, L1] – monocarbonyl or dicarbonyl compound [(O)-ligson, L2] ( $M = VO, Cr, Mn, Fe, Co, Ni, Cu, Zn, L1$  – ethanedithioamide-1,2  $H_2N-C(S)-C(S)-NH_2$ , L2 – methanal  $CH_2O$  or propanone  $H_3C-C(O)-CH_3$ ) using DFT B3LYP hybrid method with 6-31G(d) basis set and Gaussian 98 program, are presented. Coordinates of all atoms contained in «template» metallocomplexes, the lengths of bonds, valence and torsion angles between various atoms were calculated. An unusual character of change of these parameters depending on M nature, is noted and, also, the fact that N–C–O–C–N and N–C–C–C–N groups of six-numbered metalcycles contained in given complexes, are not in the same flatness with  $MN_2S_2$  groups is discussed.*

**Keywords:** Macrocylic complex, template synthesis, molecular structure, DFT B3LYP method.

## Introduction

One of the most important methods of obtaining of metallomacrocylic coordination compounds is template synthesis where macrocylic ligand is formed from simple acyclic organic compounds (ligand synthons or ligsons). This method allows to obtain the metallocomplexes, the synthesis of which by traditional methods is either difficult or impossible.<sup>[1-5]</sup> As a rule, template synthesis is accompanied with considerable decrease of entropy of reaction and proceeds under rather hard conditions. This synthesis may be facilitated by using biopolymer-immobilized matrix systems providing preliminary decrease of entropy of reactionary medium.<sup>[6-8]</sup> One of the ligsons in given process (L1) may be organic compound containing two (C=S) groups and N donor atoms, for example ethanedithioamide-1,2,  $H_2N-C(=S)-C(=S)-NH_2$ , or propanedithioamide-1,3,  $H_2N-C(=S)-CH_2-C(=S)-NH_2$ . As another ligson (L2), some organic compounds containing one or two carbonyl groups (C=O), may be used, for example methanal  $H_2C=O$ , propanone  $H_3C-C(=O)-CH_3$ , ethanedial-1,2  $HC(=O)-CH(=O)$ , etc. The fact of template synthesis into triple systems containing  $M^{II}$  ion ( $M = Co, Ni, Cu$ ), ligand synthons L1 and L2 indicated, was evidenced before in<sup>[9-13]</sup>. Also, some details related to coordination of corresponding macrocylic ligand to metal ion in metallocomplexes formed as a result of such a template synthesis, were ascertained. However, space structure of these complexes has not been reliably established up to now. The point is that their isolation in crystalline form suitable for X-ray diffraction analysis, is extremely difficult. In this connection, non-empirical quantum-chemical calculation of structure of metallomacrocylic coordination compounds formed in the [ $M^{II}$ – L1– L2] triple systems, becomes particularly actual.

One of the most suitable methods for such a calculation is hybrid method of the density functional theory B3LYP (further DFT B3LYP) with 6-31G(d) basic set<sup>[14,15]</sup> which was successfully used in many works published before.

The simplest of triple systems indicated are [ $M^{II}$  ion – ethanedithioamide-1,2 – methanal] and [ $M^{II}$  ion – ethanedithioamide-1,2 – propanone]. The present paper is devoted to namely these systems. Quantum-chemical calculation of metallocomplexes formed as a results of template reactions in the given systems with using DFT B3LYP method, was carried out by us for the first time.

## Method

DFT B3LYP level of theory<sup>[14]</sup> was used by us for calculations. It is hybrid DFT method using Becke function (1988) including Slater exchange, by beginning with amendment including density gradient, and correlation function of Lee, Yang and Parr, which includes local and non-local terms.

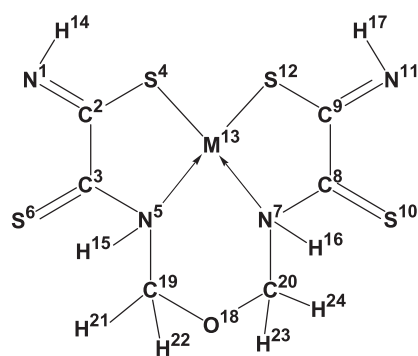
The energy values  $E$  were calculated according to Equation 1, where  $V$  is nuclearic energy of repulsion,  $\langle hP \rangle$  – one-electronic (kinetic + potential) energy,  $1/2\langle PJ(P) \rangle$  – energy of electrons repulsion,  $EX[P]$  – exchange function;  $EC[P]$  – correlation function.

$$E = V + \langle hP \rangle + 1/2\langle PJ(P) \rangle + EX[P] + EC[P] \quad (1)$$

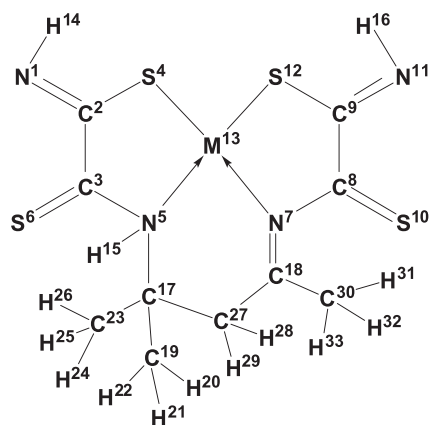
6-31G(d) basis set where each inner atom orbital (AO) is described by six functions of Gauss type (GTO), valence 2s- AO – by three GTO, valence p-AO – by one GTO, with addition of polarization d-GTO to each p-function, was used. All calculations were made with using Gaussian 98 program.<sup>[15]</sup>

According to the published experimental data,<sup>[9-12]</sup> (N,N,S,S)-coordination of donor centers of template ligand to metal ion occurs in the complexes formed in the [ $M^{II}$ – ethanedithioamide-1,2 – methanal] and in the [ $M^{II}$ – ethanedithioamide-1,2 – propanone]

### (5.6.5) Macrotricyclic Complexes



Complex 1



Complex 2

triple systems (M= Co, Ni, Cu). In this connection, the following structures of complexes which may be theoretically expected as a result of possible template reactions in the triple systems indicated, were considered in our work (atoms numbering is shown by figures; M= VO, Cr, Mn, Fe, Co, Ni, Cu, Zn).

We have calculated the geometrical parameters of the structure of these complexes for each of M<sup>II</sup> ions indicated above

(Cartesian coordinates of all atoms, length of bonds, valence and torsion angles between various atoms).

## Results and Discussion

According to data of these calculations, metalmacrotricyclic complexes **1** as well as complexes **2** of Mn<sup>II</sup>, Fe<sup>II</sup> and Co<sup>II</sup> are high-spin complexes (spin multiply of basic state is 6, 4 and 3, respectively). The basic states of Cu<sup>II</sup> and Zn<sup>II</sup> compounds **1** and **2** are spin doublet and spin singlet, respectively. Ni<sup>II</sup> complex of type **1** is paramagnetic and has  $M_S$  value = 3; however, Ni<sup>II</sup> complex of type **2** is diamagnetic and has  $M_S = 1$ . The data concerning energies of states with various  $M_S$  is presented in the Tables 1-2.

The data on (N,N,S,S) coordination to M in complexes **1** and **2** are presented in the Table 3. As may be seen, various types of planar or tetrahedral coordination of donor centers of macrocyclic ligand occur to be depending on the metal nature. The examples of space structures of complexes considered are shown in Figures 1, 2. The change of M–N and M–S bonds lengths depending on M nature are shown in Figures 3, 4; separate valence and torsion angles - in Figures 5-8. The data of Figures 3-4 bear testimony that M–N and M–S bonds lengths in the complex **1** as well as in the complex **2** are rather considerably distinguished. Moreover, the lengths of two M–N bonds [M(13)N(5) and M(13)N(7)] and two M–S bonds [M(13)S(4) and M(13)S(12)] distinguished between themselves, too. This distinction is more noticeably pronounced in the case of complexes **2**; most sharply it develops for M–N bonds in the complexes of Ni<sup>II</sup> and Zn<sup>II</sup> [in the case of Zn<sup>II</sup>, the distinction between of two M–N bonds surpasses 40 pm (213.7 and 257.3 pm, respectively)], for M–S bonds, in the Co<sup>II</sup> complex. As it may be seen from the Figure 3, in complexes of type **1**, the most long and the most short M–N bonds are observed in the case of Mn<sup>II</sup> and Zn<sup>II</sup>, the most long and the most short M–S bonds – in Mn<sup>II</sup> and Ni<sup>II</sup> complexes, respectively. In the

**Table 1.** Relative energies in basic and in highly excited states with various  $M_S$  values in metalmacrotricyclic compounds of type **1**.

M <sup>II</sup>	Electron configuration	Relative energies for states with various spin multiply $M_S$ , kJ/mole *					
		1	2	3	4	5	6
Mn <sup>II</sup>	3d <sup>5</sup>	-	171.5	-	92.5	-	0
Fe <sup>II</sup>	3d <sup>6</sup>	198.5	-	19.5	-	0	-
Co <sup>II</sup>	3d <sup>7</sup>	-	15.6	-	0	-	107.1
Ni <sup>II</sup>	3d <sup>8</sup>	30.4	-	0	-	-	-
Cu <sup>II</sup>	3d <sup>9</sup>	-	0	-	117.6	-	-
Zn <sup>II</sup>	3d <sup>10</sup>	0	-	135.3	-	-	-

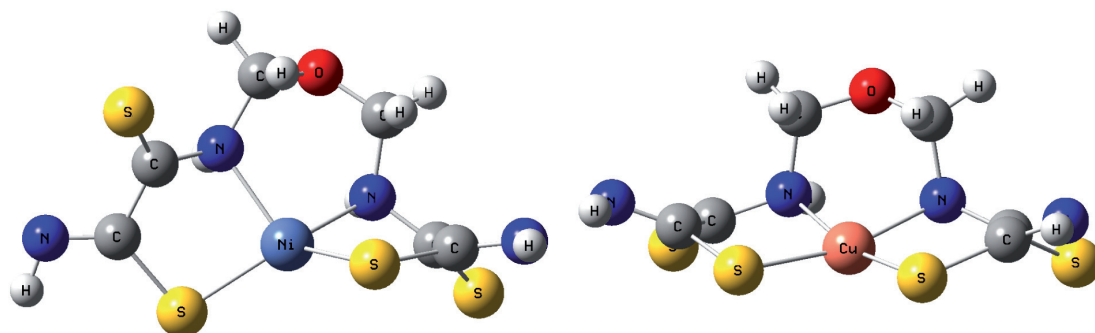
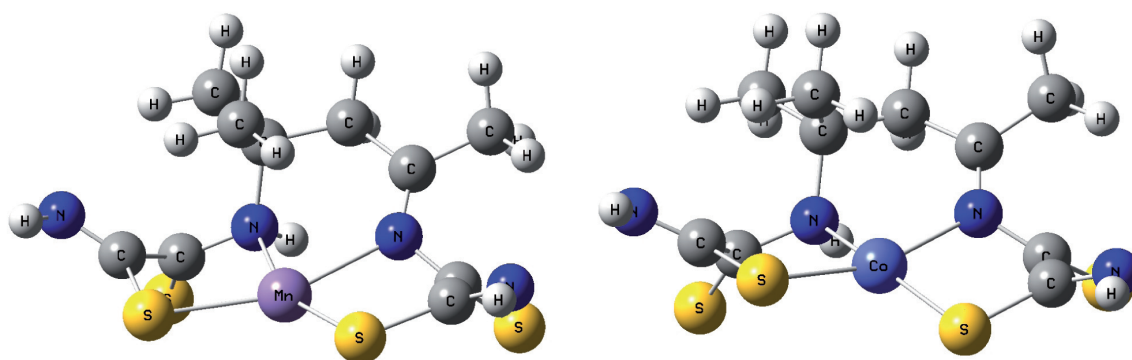
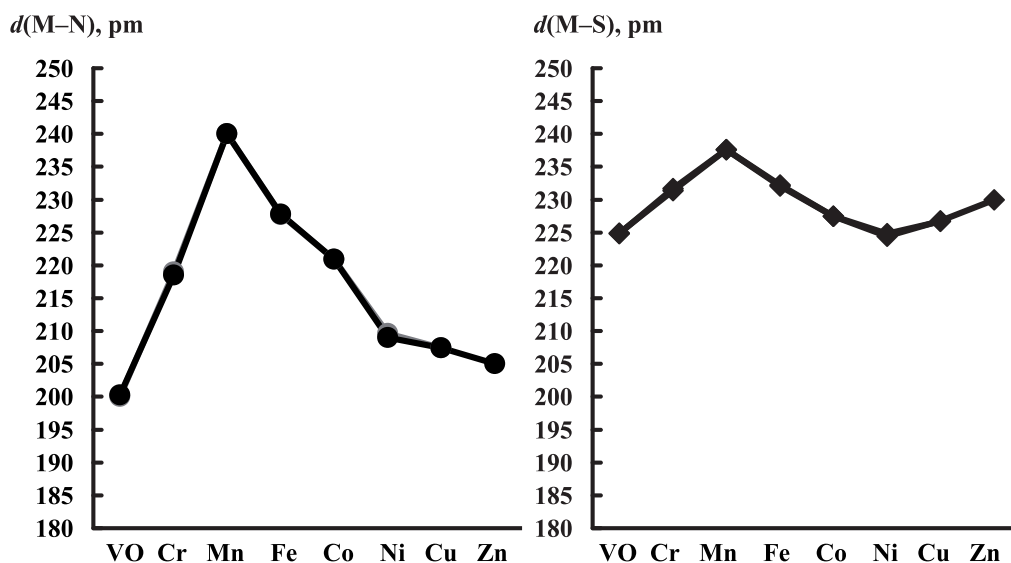
**Table 2.** Relative energies in basic and in highly excited states with various  $M_S$  values in metalmacrotricyclic compounds of type **2**.

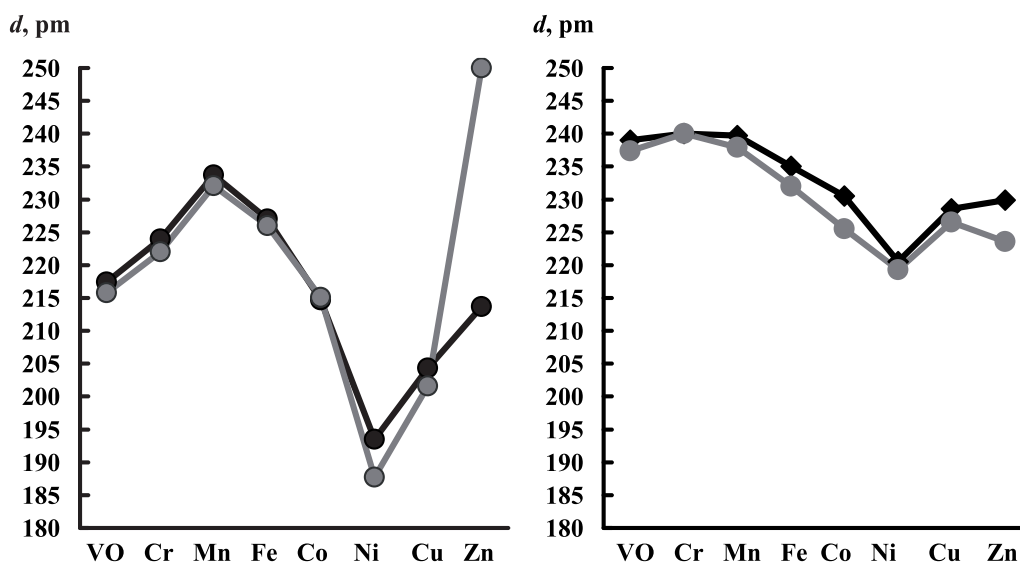
M <sup>II</sup>	Electron configuration	Relative energies for states with various spin multiply $M_S$ , kJ/mole *					
		1	2	3	4	5	6
Mn <sup>II</sup>	3d <sup>5</sup>	-	158.9	-	43.0	-	0
Fe <sup>II</sup>	3d <sup>6</sup>	158.2	-	10.8	-	0	-
Co <sup>II</sup>	3d <sup>7</sup>	-	10.3	-	0	-	81.3
Ni <sup>II</sup>	3d <sup>8</sup>	0	-	25.6	-	-	-
Cu <sup>II</sup>	3d <sup>9</sup>	-	0	-	93.9	-	-
Zn <sup>II</sup>	3d <sup>10</sup>	0	-	65.7	-	-	-

\* “ – “ non-existing spin states for given M<sup>II</sup>.

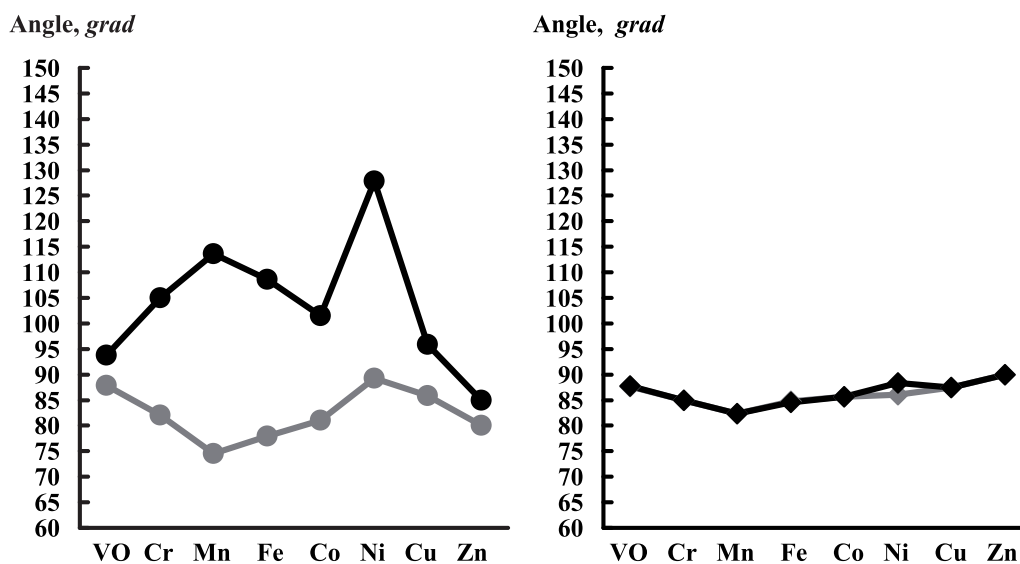
**Table 3.**  $M_S$  values of basic state and  $(N,N,S,S)$  coordination to M in complexes **1** and **2** for various metals.

M	Complex 1		Complex 2	
	$M_S$	$(N,N,S,S)$ coordination to M	$M_S$	$(N,N,S,S)$ coordination to M
VO	2	Plane	2	Tetragon-pyramidal
Cr	5	Quasi-plane	5	Plane
Mn	6	Quasi-plane	6	Quasi-plane
Fe	5	Quasi-plane	5	Quasi-plane
Co	4	Quasi-plane	4	Quasi-tetrahedral
Ni	3	Quasi-tetrahedral	1	Plane
Cu	2	Plane	2	Plane
Zn	1	Quasi-tetrahedral	1	Quasi-planar

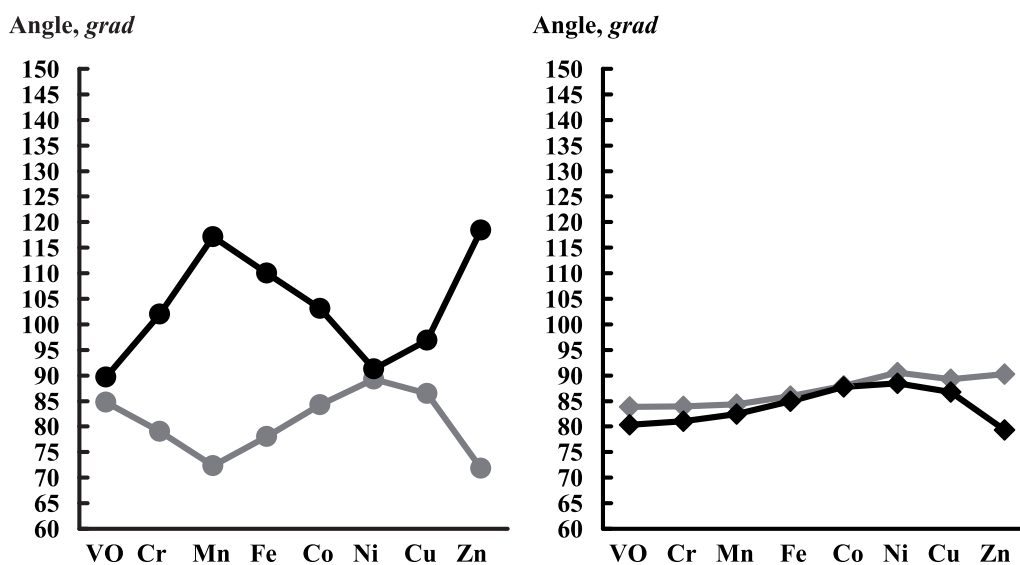
**Figure 1.** The space structure of complexes **1**: Ni<sup>II</sup> (left) and Cu<sup>II</sup> (right).**Figure 2.** The space structure of complexes **2**: Mn<sup>II</sup> (left) and Co<sup>II</sup> (right).**Figure 3.** Changes of length of M-S and M-N bonds for template complexes formed in M<sup>II</sup>-ethanedithioamide-1,2 – methanal systems: Left: M(13)-N(5) (black), M(13)-N(7) (grey), Right: M(13)-S(4) (black), M(13)-S(12) (grey).



**Figure 4.** Changes of length of M-S and M-N bonds for template complexes formed in  $M^{II}$  – ethanedithioamide-1,2 – propanone systems. *Left:* M(13)-N(5) (black), M(13)-N(7) (grey), *Right:* M(13)-S(4) (black), M(13)-S(12) (grey).



**Figure 5.** Changes of valence angles for template complexes formed in  $M^{II}$  – ethanedithioamide-1,2 – methanal systems. *Left:*  $\angle MNM$  (black),  $\angle SMS$  (grey), *Right:*  $\angle S(4)M(13)N(5)$  (black),  $\angle N(7)M(13)S(12)$  (grey).



**Figure 6.** Changes of valence angles for template complexes formed in  $M^{II}$  – ethanedithioamide-1,2 – propanone systems. *Left:*  $\angle MNM$  (black),  $\angle SMS$  (grey), *Right:*  $\angle S(4)M(13)N(5)$  (black),  $\angle N(7)M(13)S(12)$  (grey).

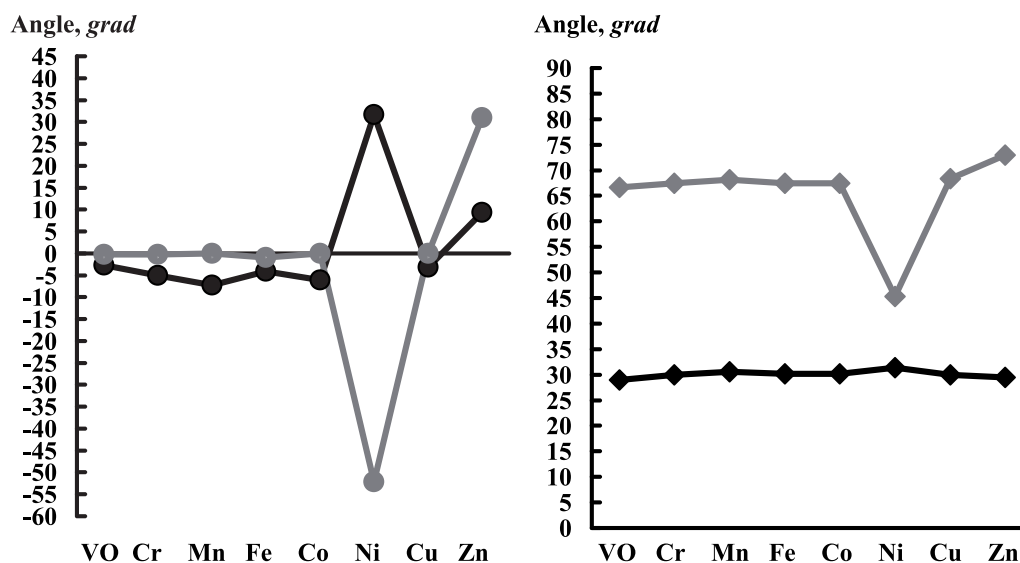
complexes of type **2**, the most long and the most short length bond for both M–N and M–S bonds are observed in the case of Mn<sup>II</sup> and Zn<sup>II</sup> complexes (Figure 4).

The dynamics of changes of N(5)M(13)N(7), S(4)M(13)S(12), S(4)M(13)N(5) and S(12)M(13)N(7) valence angles for various M in the complexes considered is once more interesting (Figures 5-6). It is noteworthy that the values of N(5)M(13)N(7) and S(4)M(13)S(12) angles very strongly depend on M nature whereas the values of S(4)M(13)N(5) and S(12)M(13)N(7) angles – comparatively small distinguished between themselves. It may be believed in this connection that the «bite» of the N–C–C–S ligating moieties remains relatively constant as one would expect (hence, the angle S–M–N remains constant), and that the two approximate chelating plans formed by the two ethanedithioamide moieties can indeed twist with respect to each other (taking advantage of the chain of  $\sigma$ -bonds connecting them), leading towards tetrahedral geometries and therefore affecting the N–M–N and S–M–S angles. The magnitude of these changes is indeed expected to mirror the tendency of these metals to leave the square-planar geometry and adopt tetrahedral geometry. The character of change of N(5)M(13)N(7) angle values in the case of complex **1** leaps to the eye in the ordinary sense of the word – from VO to Mn these values increase, from Mn to Co – decrease, from Co to Ni – sharply increase and from Ni to Zn – sharply decrease (Figure 5, left). In the case of complex **2**, on the contrary, for Ni this angle has a minimum (Figure 6, left). The curves of change of values of S(4)M(13)S(12) angle, however, is similar for these complexes (Figures 5, 6) and may be considered as «mirror reflection» of curves of change of N(5)M(13)N(7) angle for complexes **2**: minimal value of it occurs for Mn<sup>II</sup>, maximal one – for Ni. It should be noted in this connection that in the case of Ni<sup>II</sup> complex **2** the angles N(5)M(13)N(7) and S(4)M(13)S(12) are practically equally (91.3 and 89.3°, respectively). The distinction between S(4)M(13)N(5) and S(12)M(13)N(7) valence angles for various M in these complexes shows itself in considerably lesser degree (Figures 5-6); it is extremely appreciable only for Zn<sup>II</sup> complex of type **2** (Figure 6, right).

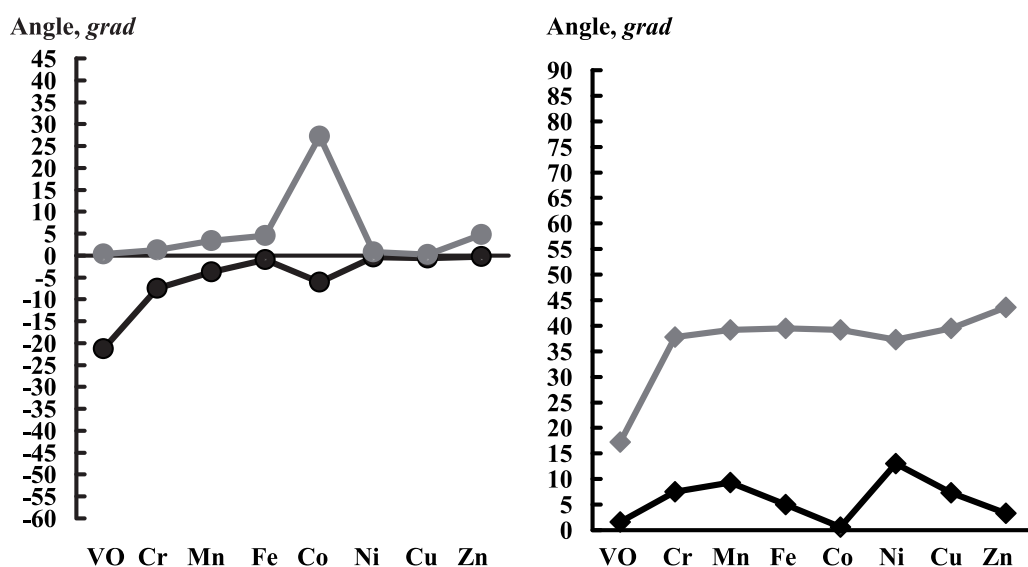
It is also interesting to see the dynamics of change of valence N(5)M(13)N(7), S(4)M(13)S(12), S(4)M(13)N(5) and S(12)M(13)N(7) angles sum (VAS) (Figures 7-8) because given parameter may be as criterion of degree of departure of MN<sub>2</sub>S<sub>2</sub> chelate grouping of atoms from the plane structure. As may be seen from the Figures 7-8, almost for all complexes of types **1** and **2** (VAS-360°) is negative and, besides, as a rule, its absolute value is lesser than 10°. Sole exception to this rule is Ni<sup>II</sup> complex of type **1** where (VAS-360°) is 31.7°. The values of torsion angles N(5)S(4)S(12)N(7), N(5)N(7)C(20)O(18), N(5)M(13)N(7)C(20) in the case of complex **1** and N(5)S(4)S(12)N(7), N(5)N(7)C(18)C(27), N(5)M(13)N(7)C(18) – in the case of complex **2**, which are presented in the Figures 7, 8, testify to that six-numbered chelate cycles N(5)–C(19)–O(18)–C(20)–N(7) (in complexes of type **1**) and N(5)–C(17)–C(27)–C(18)–N(7) (in complexes of type **2**) are not in the same flatness with MN<sub>2</sub>S<sub>2</sub> grouping. Moreover, these cycles are not plane themselves – oxygen atom O(18) (in the complex **1**) and carbon atom C(27) (in the complex **2**) are deflected from flatness of N–C–C–N atoms on rather considerable angles. And so, in anyone of these complexes chelate macrocycle is not plane.

## Conclusions

To summarize the aforesaid, it may be ascertained that any of (5.6.5) macrotricyclic M<sup>II</sup> complexes with ligands arising as a result of template reactions in the M<sup>II</sup> – ethanedithioamide-1,2 – methanal and M<sup>II</sup> – ethanedithioamide-1,2 – propanone triple systems, as a whole, is not plane. Moreover, MN<sub>2</sub>S<sub>2</sub> metalchelate junction is not strictly plane, too, because for the each of complexes **1** and **2** the values of sum of valence angles (VAS) is not equal exactly 360° (although VAS-360° values, as a rule, are relatively small – lesser than 10°). The first as well as the second is a little unexpected thing because, *a priori*, it should be expected that all these complexes considered would have coplanar structure. It is noteworthy in this connection that additional metalcycles formed as a result of template “stitching”, are not plane



**Figure 7.** Changes of valence angles sum (VAS) and torsion angles for template complexes formed in M(II)– ethanedithioamide-1,2 – methanal systems. *Left:* (VAS-360°) (black),  $\angle$ N(5)S(4)S(12)N(7) (grey), *Right:*  $\angle$ N(5)N(7)C(20)O(18) (black),  $\angle$ N(5)M(13)N(7)C(20) (grey).



**Figure 8.** Changes of valence angles sum (VAS) and torsion angles for template complexes formed in  $M^{II}$  – ethanedithioamide-1,2 – propanone systems. *Left:* (VAS-360°) (black),  $\angle N(5)S(4)S(12)N(7)$  (grey), *Right:*  $\angle N(5)M(13)N(7)C(18)$  (black),  $\angle N(5)N(7)C(18)C(27)$  (grey).

themselves, too – oxygen atom (in the complex **1**) and carbon atom (in the complex **2**) are deflected from flatness of N–C–C–N atoms on rather considerable angles. Both complexes **1** and complexes **2** are strongly asymmetric and, at the best, have only one element of symmetry, namely symmetry plane passing through M atom and O (in the case of complexes **1**) or C (in the case of complexes **2**) atom contained in 6-membered metalchelate cycles.

Finally, it may be noted that the character of change of bonds lengths, of valence and torsion angles in the complexes **1** and **2** under examination is unusual and cannot be adequately interpreted at the present time. Some details may be understood somehow [for example,  $d(M-N)$  and  $d(M-S)$  values which reach of maximum for  $Mn^{II}$ , may be connected with availability of  $Mn^{II}$  of half-filled electron configuration  $3d^5$ ] but most of the data obtained by us, demand a special consideration and subsequent researches. These and similar data are certain interest for structural coordination chemistry of macrocyclic complexes, the more so that experimental determination of molecular structures of compounds considered in the given paper is so far extremely difficult thing.

**Acknowledgements.** The Russian Foundation of Basic Researches (RFBR), grant No 09-03-97001, is acknowledged for financial support. Also, authors are grateful to Supercomputer Center of Kazan Scientific Center of Russian Academy of Sciences where all quantum-chemical calculations were carried out.

## References

1. Bush D.H. *Adv. Chem. Ser.* **1963**, *37*, 1-18.
2. *Coordination Chemistry of Macrocyclic Compounds* (G.A. Nelson, Ed.) Plenum Press: New York – London, **1979**. 664 p.
3. Bush D.H. *Uspekhi Khim.* **1969**, *38*, 822-853 (in Russ.).
4. *Synthesis of Macrocycles. The Design of Selective Complexing Agents* (R.M. Izatt, Y.Y. Christiansen, Eds.) Plenum Publishing, New York, **1987**. 447 p.
5. Gerbeleu N.V., Arion V.B., Burgess J. *Template Synthesis of Macrocyclic Compounds*. Wiley – VCH, Weinheim – New York – Chichtster – Brisbane – Singapore – Toronto, **1999**. 565 p.
6. Mikhailov O.V. *Gelatin-Immobilized Metalcomplexes*. Scientific World, Moscow, **2004**. 236 p. (in Russ.).
7. Mikhailov O.V., Kazymova M.A., Shumilova T.A. *Transit. Met. Chem.* **2007**, *32*, 1056-1060.
8. Mikhailov O.V. *J. Coord. Chem.* **2008**, *61*, 1333-1384.
9. Mikhailov O.V. *Int. J. Inorg. Mater.* **2001**, *3*, 1053-1061.
10. Mikhailov O.V. *Transit. Met. Chem.* **2000**, *25*, 552-558.
11. Mikhailov O.V., Khamitova A.I. *Transit. Met. Chem.* **2000**, *25*, 26-31.
12. Mikhailov O.V., Kazymova M.A., Shumilova T.A., Vafina L.R. *Heterocyclic Commun.* **2000**, *6*, 357- 362.
13. Mikhailov O.V., Khamitova A.I. *Russ. J. Coord. Chem.* **1998**, *24*, 629-634.
14. Becke A.D. *J. Chem. Phys.* **1993**, *98*, 1372-1378.
15. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery J.A., Stratmann Jr. 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 M.A., Nanayakkara A., Gonzalez C., Challacombe C., 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. *Gaussian 98*. Gaussian Inc., Pittsburgh, **1998**.

Received 14.01.2010

Accepted 06.07.2010

First published on the web 27.09.2010