DFT STUDY ON THE RELATIVE STABILITY OF ISOMERIC MACROCYCLIC METAL CHELATES OF DIVALENT 4*d*-ELEMENT IONS WITH TETRADENTATE (NSSN)- AND (NNNN)-"TEMPLATE" LIGANDS

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Using the density functional method (DFT) in the OPBE/TZVP//QZP approximation and the Gaussian09 program, geometric parameters and total energies of molecular structures of the Mo(II), Tc(II), Ru(II), Rh(II), Pd(II), Ag(II) and Cd(II) macrotricyclic complexes with (NSSN)- and (NNNN)-coordinations of the ligand donor centers to the complex, arising as a result of complexing between M(II) indicated above, dithiooxamide $H_2N–C(= S)–C(= S)–NH_2$ and glyoxal $HC(=O)–CH(=O)$, were calculated. Based on the data of this calculation, it is shown that in the case of Mo(II), Tc(II), Ru(II), Rh(II) and Pd (II) complexes with (NSSN)-coordination of ligand are more stable, whereas in the case of Ag(II) and Cd(II), with (NNNN)-coordination; in addition, for the Mo(II) and Ru(II) complexes, a pseudo-tetrahedral environment of the central metal ion takes place by donor atoms, while for the complexes Tc(II), Rh(II), Pd(II), Ag(II), and Cd(II) are planar ones. The bond lengths and bond angles in the indicated coordination compounds are given and it is noted that the Ag(II) and Cd(II) complexes are almost flat, the Tc(II), Rh(II), and Pd(II) complexes are small, while the Ru(II), a fairly significant deviation from coplanarity. The five-membered metal chelate cycles formed as a result of complexing, in most of these complexes are either practically flat, or exhibit a slight (within 5°) deviation from coplanarity; the only exceptions are the Mo(II) and Ru(II) complexes.
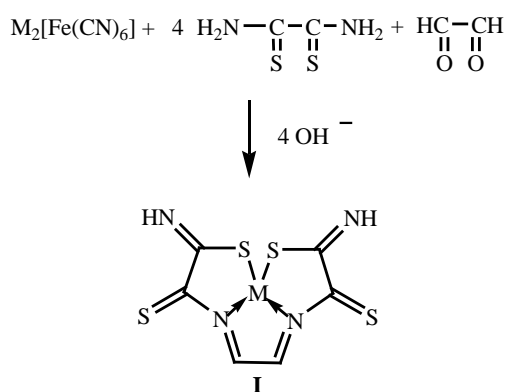
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INTRODUCTION

We experimentally recorded template synthesis of (555)macrotricyclic metal complexes (**I**) in the ternary systems M(II)-dithiooxamide $[H_2N–C(=S)–C(=S)–NH_2]$ and glyoxal $[CH(=O)–CH(=O)]$ (M=Co, Ni, Cu), proceeding according to Scheme 1 in the $Co_2[Fe(CN)_6]^-$, $Ni_2[Fe(CN)_6]^-$ and $Cu_2[Fe(CN)_6]^-$-gelatin-immobilized matrix implants.[1-5]

Scheme 1. Formation of "template" complex of type **I.**

Based on the data of various physicochemical methods, it was also shown that the ligand contained in each of these complexes namely, 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8, is tetradentate and coordinated to any of the above M(II) through two donor nitrogen atoms and two donor sulfur atoms. It should be noted in this connection that such a tetradentate ligand is in principle capable of coordinating to M(II) in a slightly different way, namely, through four donor nitrogen atoms and, together with the type **I** complexes where (NSSN)-coordination of 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8 to M(II) ion takes place, also forms complexes of type **II** isomeric to complexes of type **I** (Figure 1) in which, (NNNN)-coordination of the ligand indicated above, occurs.
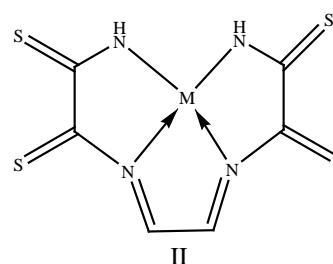

Figure 1. Structure of "template" complex of type **II**.

A quantum chemical calculation of the molecular structures of complexes of type **I** with 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1.8 and (NSSN)-coordination of chelate ligand was carried out using the DFT method as the above-mentioned M(II) ions, as well as three other M(II) of 3*d* elements, namely Mn(II), Fe(II) and Zn(II).[6,7] In subsequent works,[8,9] the fundamental possibility of the existence of complexes **I** and **II** of similar

composition containing M(II) ions of $4d$ elements, Mo(II), Tc(II), Ru(II), Rh(II), Pd(II), Ag(II), and Cd(II) was shown. However, in these works, the question of that which of these isomeric macrocyclic metal chelates – with (NSSN) or with (NNNN) coordination is more energetically favorable in the case of $4d$ element M(II) complexes, as well as the extent to which this depends on the nature of M(II) and the interpretation of this dependence, remained outside the scope of consideration. In this connection, the given article will be devoted to the consideration of namely these questions.

CALCULATION METHOD

To carry out quantum-chemical calculations, we in this work used the DFT method using the non-hybrid OPBE functional described in[10,11] with the basis set TZVP for H, C, N, O, and S atoms and the basis set QZP for the corresponding atom $4d$-element M.[12-14] The calculations were performed by using the Gaussian09 program.[15] As in our earlier works,[7-9,16-21] the correspondence of the found stationary points to energy minima in all cases was proved by calculating the second derivatives of energy with respect to atomic coordinates; besides, all equilibrium structures corresponding to minimum points on the potential energy surfaces, had only positive values of frequencies. For Mo(II) complexes having $4d^4$ electron configuration, multiplicities 1, 3, 5 and 7, for Tc(II) complexes ($4d^5$), 2, 4 and 6, for Ru(II) ones ($4d^6$), 1, 3 and 5, for Rh(II) ones ($4d^7$), 2, 4 and 6, for Pd(II) ones ($4d^8$), 1, 3 and 5, for Ag(II) ones ($4d^9$), 2, 4 and 6, and for Cd(II) ones ($4d^{10}$), 1 and 3, were considered. Of the structures optimized for the indicated multiplicities, the structure having the lowest energy, was chosen for each of these complexes. The calculation of the parameters of molecular structures with multiplicities other than 1 was always carried out by the unlimited method (*UOPBE*); with multiplicity 1, by the restricted method (*ROPBE*). For multiplicity 1, an unlimited method of calculation was also used, in combination with the option GUESS = Mix; in this case, the results obtained were always similar to the results obtained using the restricted method.

RESULTS AND DISCUSSION

According to the data of our quantum-chemical calculation in the aforementioned DFT method version, the complexes of all the ions of the M(II) $4d$ elements named above with 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1.8 of type **I** as well as of type **II** are in principle capable of independent existence. The molecular structures of these metal macrocyclic compounds are presented in figures 2 and 3, the key parameters of these structures (bond lengths and bond angles) are given in Tables SM1-SM2 (see *Supplemental Materials*). Total energies of complexes under study are presented in the Table 1. The Mo(II), Tc(II), Ru(II), Rh(II), and Pd(II) complexes of type **I** are more stable, in terms of energy, than the complexes of type **II**, whereas for complexes of Ag(II) and Cd(II), the inverse relationship is operative. Even more interesting is that when moving from Mo(II) to Ru(II), the values of [$E(\mathbf{II})$–$E(\mathbf{I})$] increase, and when moving from Ru(II) to Pd(II), on the contrary, they decrease while remaining positive; upon

transition from Pd(II) to Ag(II) and further to Cd(II) [$E(\mathbf{II})$–$E(\mathbf{I})$] not only changes in sign, but also increases sharply in absolute value (Table 1). The relative energies of the ground and excited states with different spin multiplicities (MS) of complexes **I** and **II** for different M(II) in the gas phase are presented in Table 2.

Table 1. Total energies (taking into account the zero-point energy) of complexes $E(\mathbf{I})$ and $E(\mathbf{II})$ for various M(II) in the gas phase.

M(II)	$E(\mathbf{I})$	$E(\mathbf{II})$
Mo(II)	-6021.249119 **[0.0]**	-6021.237988 **[29.2]**
Tc(II)	-6250.771513 **[0.0]**	-6250.760050 **[30.1]**
Ru(II)	-6487.654750 **[0.0]**	-6487.635976 **[49.3]**
Rh(II)	-6732.074667 **[0.0]**	-6732.063863 **[28.4]**
Pd(II)	-6984.231040 **[0.0]**	-6984.229051 **[5.2]**
Ag(II)	-7243.989341 **[60.6]**	-7244.012438 **[0.0]**
Cd(II)	-7511.621916 **[66.9]**	-7511.647408 **[0.0]**

Values without parentheses are total energies in Hartree units, in square brackets, relative energies in kJ mol^{-1} (the total energy of the complex with the lowest value of E is taken as 0.0 in all cases).

Table 2. Relative energies of the ground and excited states with different M_S of complexes **I** and **II** with various M(II) in the gas phase in kJ/mol

M(II)	I	II
Mo(II)	$M_S = 1$ (-) *	$M_S = 1$ (48.7)
	$M_S = 3$ (0.0)	$M_S = 3$ (0.0)
	$M_S = 5$ (42.9)	$M_S = 5$ (29.0)
	$M_S = 7$ (161.6)	$M_S = 7$ (137.4)
Tc(II)	$M_S = 2$ (13.3)	$M_S = 2$ (35.2)
	$M_S = 4$ (0.0)	$M_S = 4$ (0.0)
	$M_S = 6$ (40.8)	$M_S = 6$ (7.6)
Ru(II)	$M_S = 1$ (10.8)	$M_S = 1$ (0.0)
	$M_S = 3$ (0.0)	$M_S = 3$ (9.0)
	$M_S = 5$ (11.9)	$M_S = 5$ (120.2)
Rh(II)	$M_S = 2$ (16.4)	$M_S = 2$ (13.1)
	$M_S = 4$ (0.0)	$M_S = 4$ (0.0)
	$M_S = 6$ (153.8)	$M_S = 6$ (102.0)
Pd(II)	$M_S = 1$ (3.1)	$M_S = 1$ (3.9)
	$M_S = 3$ (0.0)	$M_S = 3$ (0.0)
Ag(II)	$M_S = 2$ (0.0)	$M_S = 2$ (0.0)
	$M_S = 4$ (177.6)	$M_S = 4$ (100.2)
	$M_S = 6$ (302.1)	$M_S = 6$ (215.0)
Cd(II)	$M_S = 1$ (4.2)	$M_S = 1$ (39.5)
	$M_S = 3$ (0.0)	$M_S = 3$ (0.0)

The total energy of the complex with spin multiplicity corresponding to the minimum energy is taken as 0.0 in all cases.

As can be seen from it, for the complexes of almost all the M(II) ions considered by us, the M_S values of the ground states of complexes **I** and **II** turn out to be the same; for example, the ground state of the both Rh(II) complexes is the spin quartet, so that they turn out to be high-spin

complexes; the Pd(II) and Cd(II) complexes with the ground triplet state should also be classified as such complexes. The Ag(II) complexes, in full accordance with theoretical expectations, have a spin doublet as the ground state. For the Mo(II) and Tc(II) complexes, these are the spin triplet and spin quartet, respectively, and both occupy an intermediate position between the high-spin and low-spin complexes for the electronic configurations $4d^4$ and $4d^5$, respectively. The exceptions against this background are Ru(II) complexes,
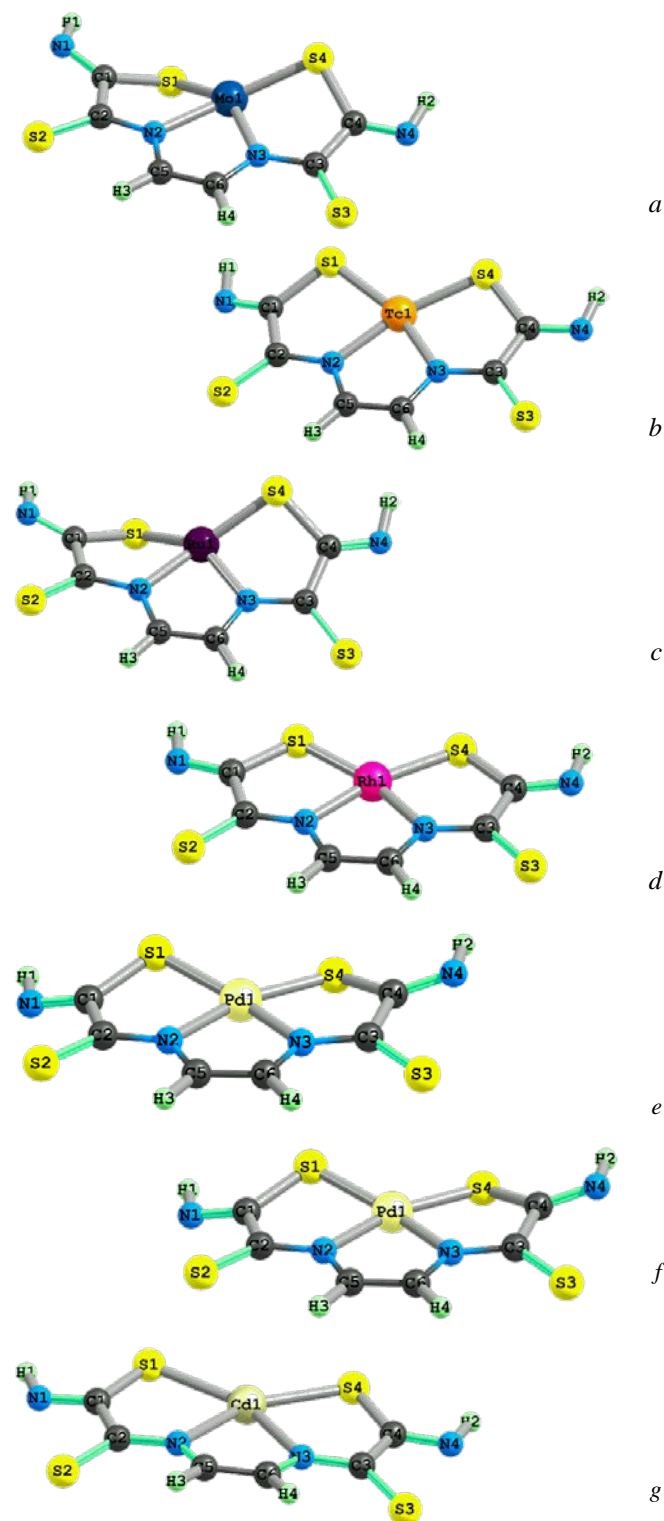

Figure 2. Molecular structures of M(II) metal chelates with (NSSN) ligand coordination: *a* – Mo(II), *b* – Tc(II), *c* – Ru(II), *d* – Rh(II), *e* – Pd(II), *f* – Ag(II), *g* – Cd(II).

Figure 3. Molecular structures of M(II) metal chelates with (NNNN) ligand coordination: *a* – Mo(II), *b* – Tc(II), *c* – Ru(II), *d* – Rh(II), *e* – Pd(II), *f* – Ag(II), *g* – Cd(II).
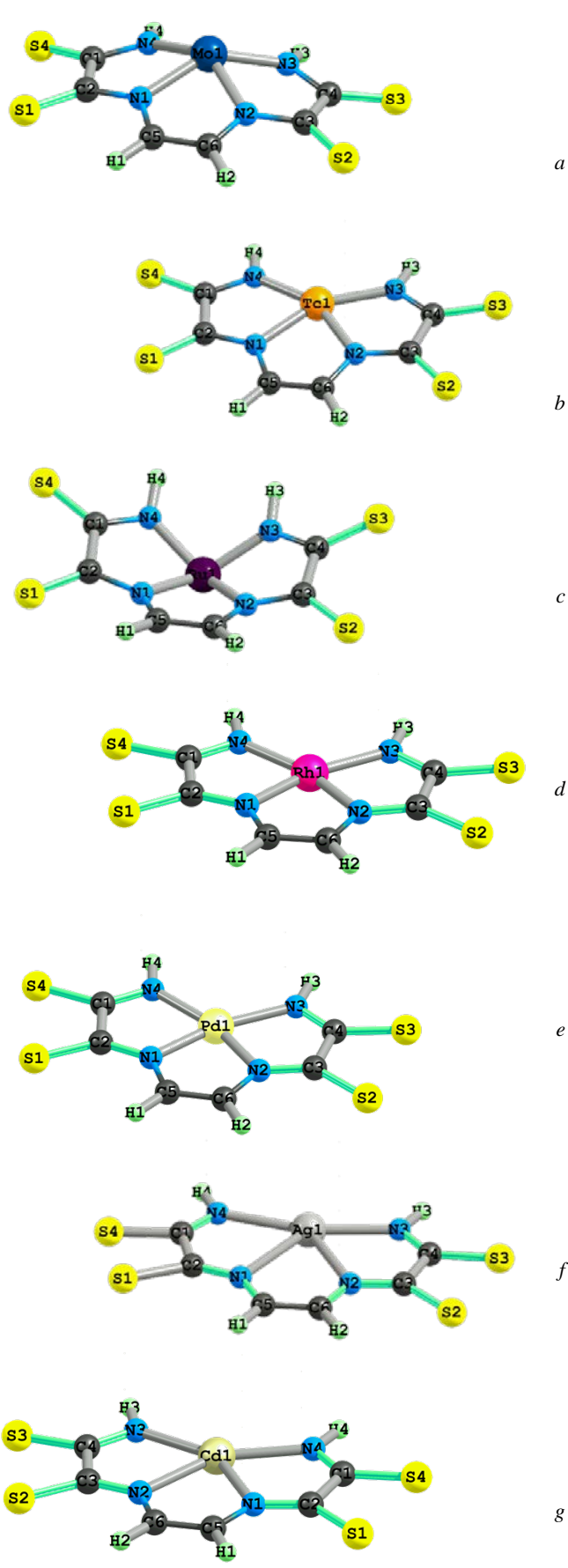
for which, in the case of complex **I**, the ground state is a spin triplet, for complex **II**, a spin singlet, so that complex **II** of this M(II) is sole low-spin complex among the coordination compounds considered by us. In connection with the foregoing, it is worth noting the curious circumstance that the cadmium(II) complex of type **II** (which, as can be seen from the data in Table 1, is significantly more stable than complex **I** isomeric to it) has a triple ground state contrary to expectations for electronic configuration $4d^{10}$ singlet state. However, our conclusions about the multiplicity of the ground state of the complexes we are considering, on the one hand, relate to the gas phase, and on the other hand, the energy difference between the triplet and singlet states in the complexes Tc(II), Ru(II), Rh(II) and especially Pd(II) is very small, and if so, it is possible that when these complexes transition to the solid phase, the states with lower values of M_S will become the main ones. Moreover, manifestations of the spin-crossover phenomenon (spin isomerism) can also be expected here.

Also, it seems interesting to look at the molecular structure of the ligand that is a part of each of the complexes under examination, namely 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8 (Figure 4).
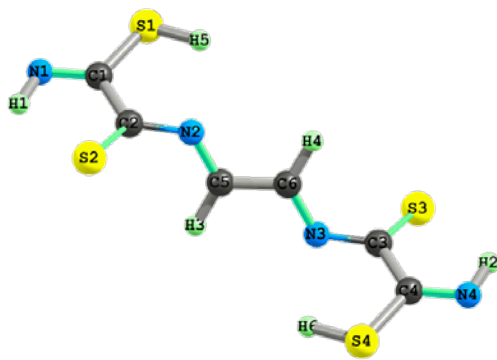

Figure 4. Molecular structures of 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8.

According to our calculation, the molecule of this ligand is very long (the distance between the most distant atoms, namely between N1 and N4, is 1042.3 pm) and at the same time is narrow (the distance between the atoms most distant from each other, namely between S1 and S2, between S3 and S4 is 437.7 pm). In contrast to the complexes formed by this ligand, it has a center of symmetry, which is located in the center of the line (C5C6) bond. It is noteworthy that the six atoms of this molecule, namely nitrogen N2, N3, carbon C5, C6, and hydrogen H3, H4 are in the one plane (!) because the dihedral angles (N2C5C6H4), (N2H4N3H3), (N2C5C6N3) and (H3C5C6H4) are equal to 0.0° or 180.0°, and the sum of the internal angles in the quadrangles (N2C6N3C5), (N2H4N3H3), (C5H4C6H3), (N2C5C6H4), (H3C5C6N3) is either 360.0° or practically does not differ from the indicated value.

It should be noted in this connection that the donor nitrogen atoms N2 and N3 are in the *trans*-position with respect to the (C5C6) bond line. That is why, for the formation of the chelate node MN_2S_2, the grouping of the atoms [H4C6N3C3(S3)C4(N4H2)S4H6] should unfold relative to the (C5C6) bond line at angle 180.0°, which is connected with certain (and considerable) energy costs. To

form the chelate node MN_4, in addition to this, the [S2C2C1(N1H1)S1H5] and [S3C3C4(N4H2)S4H6] groupings of atoms must be turned relative to the (C1C2) and (C3C4) bond lines, respectively, to the same angles 180.0°, that requires large additional energy costs. In this connection, it becomes clear that it is preferable for the ligand to form complexes with the chelate node MN_2S_2, but not with the chelate node MN_4. On the other hand, Mo(II), Tc(II), Ru(II), Rh(II), and Pd(II) ions contain the corresponding chemical elements at lower oxidation states than traditional for these elements, and belong to the category of sufficiently "soft" Pearson acids. For them, more typical is coordination to atoms with low electronegativity (in our case, to sulfur atoms). In Ag(II), silver has the same degree of oxidation II, but it is anomalously high for a given element, so this ion belongs to the category of rather "hard" Pearson acids. Therefore, coordination to atoms with high electronegativity (in our case, to nitrogen atoms) should be more probable for this M(II). As for Cd(II), it actually belongs to the category of "intermediate strength" acids and for it one can expect both (NSSN)- and (NNNN)-coordination of the ligand under consideration. Thus, the data on the coordination of the $4d$-element M(II) ions, obtained as a result of the quantum-chemical calculation, acquire a completely reasonable explanation.

CONCLUSION

As can be seen from the foregoing, for the ions of $4d$ elements under consideration, namely, Mo(II), Tc(II), Ru(II), Rh(II), Pd(II), Ag(II), and Cd(II), at complexing with 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8, formation of chelate node MN_2S_2 with coordination through two S atoms and two N atoms to the corresponding M(II), is more typical than formation of chelate node MN_4 with coordination through four N atoms. It is quite understandable, since these ions, according to Pearson's classification,[22] belong to the category of very "soft" acids and, therefore, coordination with donor atoms with relatively low electronegativity (in our case, S atoms), rather than atoms with high electronegativity (in our case, N atoms). Wherein, that is noteworthy, the difference in the total energies of structures with (NSSN) and (NNNN) coordination of the ligand to M(II) in the series Mo(II) – Cd(II) monotonically increases with the transition from Mo(II) to Ru(II) and decreases monotonically upon transition from Ru(II) to Pd(II), and in the case of Ag(II) and Cd(II), structures with a chelating site MN_4 are lower in total energy.

That is also a quite expected result due to the fact that, for Ag(II) and Cd(II), unlike the other five complexing agents M(II) considered here, coordination through donor nitrogen atoms is more characteristic in the complexes formed by them than through sulfur atoms. A significant contribution to the choice between (NSSN) and (NNNN) coordination, undoubtedly, gives the specific structure of the tetradentate chelate ligand itself (Figure 4). Nonetheless, these complexes are characterized by planar or close to it coordination of the donor centers of 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1.8 to M(II); in this case, the Rh(II), Ag(II), and Cd(II) complexes are almost flat, while the others exhibit to one degree or another a noticeable deviation from coplanarity, and this deviation is most pronounced in the Ru(II) complex.

FUNDING INFORMATION

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