ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1122–1128. © Pleiades Publishing, Ltd., 2009.
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On the Possibility of Template Synthesis in the Ternary System of Vanadium(IV)–Dithiooxamide–Formaldehyde

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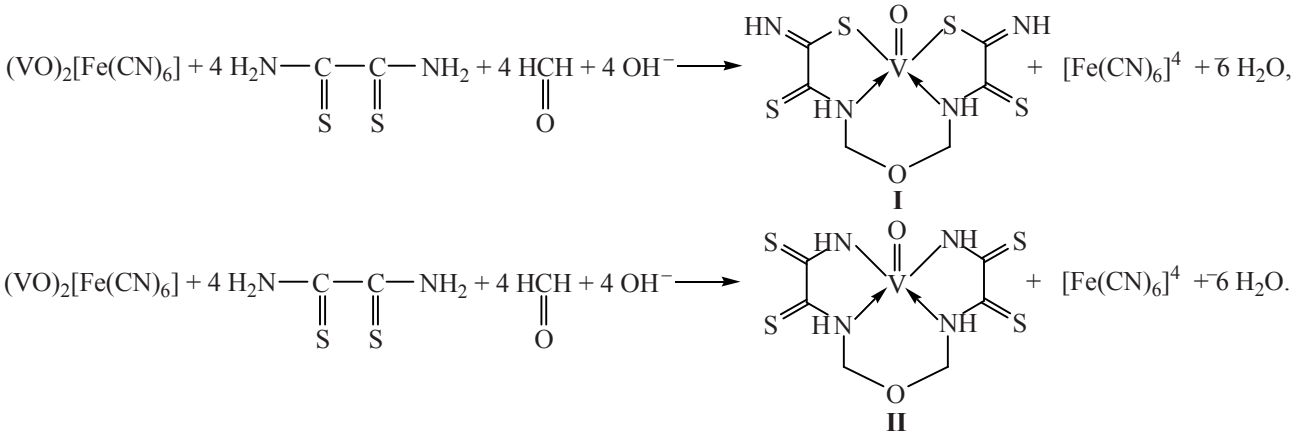
Received January 12, 2009

Abstract—With application of hybride method of density functional B3LYP with the 6-31G(d) basis set we calculated geometric parameters of macrocyclic complexes formed at the template reactions in the system V(IV)–dithiooxamide–formaldehyde of dioxovanadium(IV). The complexes are formed by tetradentate chelate ligands by means of (NNSS)- and (NNNN)-coordination of donor centers. Atomic coordinates and bond lengths of the formed complexes are listed. The values of enthalpy and Gibbs energy of the formation of the complexes are calculated and it is resumed that the template synthesis in such system can be realized at the complex formation in gelatin-immobilized matrix only.

DOI: 10.1134/S1070363209060152

Earlier has been established experimentally [1–6] proceeding of template synthesis in ternary systems including an ion M(II)–dithiooxamide–formaldehyde (M = Co, Ni, Cu), that occurs in the respective metal-hexacyanoferrate(II) gelatin-immobilized matrix implants, and some details related to coordination of the ligand formed in such synthesis with the respective metal ion. Respective data for the ternary system V(IV)–dithiooxamide–formaldehyde has not be published so far. Therefore seems actual to carry out a quantum-chemical calculation of coordination compounds that principally could form in such system due to template reactions, applying to the calculation modern non-empirical methods that allow obtaining independent objective data on their structural parameters. This communication is denoted to the presenting and discussing the results obtained in one version of such calculation, namely, with application of hybride method of density functional B3LYP.

Proceeding from the general view on the specificity of template synthesis described in [7–9], one can predict two most probable template reactions in the ternary systems of dioxovanadium(IV) hxacyanoferrate(II)–dithiooxamide–formaldehyde, leading respectively to formation of complex **I** with (NNSS)-coordination of donor centers of the "template" ligand (chelant) to V(IV), and analogous complex **II** with (NNNN)-coordination:



For each such reaction we calculated by the B3LYP 6-31G(d) method the geometric parameters of structures of the complexes **I** and **II** for the spin multiplicity of ground state $M_S = 2$ [there are no other variants of M_S here, because the highest occupied atomic orbital of V(IV) ($3d^1$ configuration) has only one unpaired electron]. Structures of these complexes obtained in our calculations are depicted in Figs. 1 and 2, the Cartesian coordinates of all atoms and bond lengths are listed in Tables 1 and 2. As follows from the calculations, principally can exist both the complexes V(IV) with (NNSS)-coordination and (VO)(IV) with (NNNN)-coordination of the chelant donor centers (**I** and **II**, respectively). Therewith, the complex **II** is energetically preferable over the complex **I** by186.4 kJ mol^{-1}, therefore at the complex formation in gas phase the formation of complex **II** is more probable. Both the complexes contain practically in one plane the sets of donor centers (NNSS) and (NNNN). In the complex with (NNSS)-coordination the angles between V–S and V–N bonds, namely, ∠S(4)V(25)N(5), ∠S(4)V(25)S(12), ∠S(12)V(25)N(7), and ∠N(7)V(25)N(5) equal to 82.57°, 87.94°, 81.65°, and 82.57°, respectively; sum of these angles equals 335.11°. In the complex with

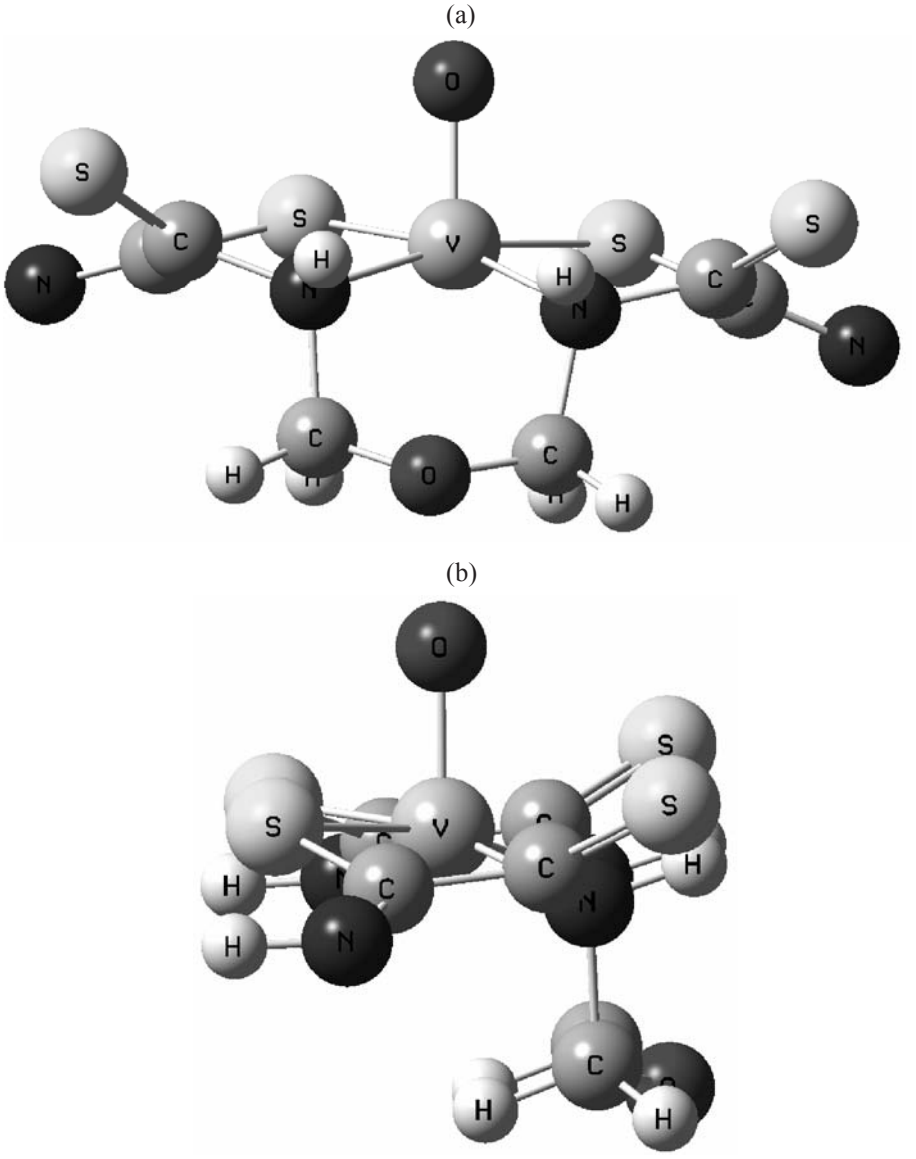


Fig. 1. Steric structure of (VO)(IV) complex of **I** type: (a) front view and (b) side view.

(NNNN)-coordination the respective angles ∠N(3)V(24)·N(15), ∠N(15)V(24)N(14), ∠N(14)V(24)N(5), and ∠N(5)V(24)N(3) equal to 75.89°, 96.91°, 75.89°, and 84.48°, respectively, their sum is 333.17°. Both these sums differ considerably from 360°. Hence, the chelate nodes VS_2N_2 and VN_4 are not planar: in both the cases the vanadium atom is slightly "elevated" above the (NNSS) and (NNNN) plans toward V=O bond (that is clearly enough seen in Figs. 1 and 2). It is significant also that the additional six-membered ring formed at the template stitching is not in the same plane as that of the donor atoms, but inclined to it rather significantly in both the cases of (NNSS)- and (NNNN)-coordination of donor centers to V(IV) (Figs. 1, 2). This ring itself is also not flat: the oxygen atom is deviated from the plane of $N–CH_2–CH_2–N$ group by a significant angle (75.12° and 79.26°, respectively). Interesting to note that the vanadium–nitrogen bond lengths *d*(V–N) for the nitrogen atoms belonging to this additional six-membered ring in both the complexes **I** and **II** are at least slightly different, but the pairs are practically the same (218.93 and 219.75 pm in complex **I**, 218.94 and 219.77 pm in complex **II**). In two complexes also are close by length the bonds vanadium–"yl" oxygen (156.65 and 157.19 pm respectively).

To solve the problem which of the above considered chelant coordination to V(IV) is advantageous, it is reasonable to consider it from the viewpoint of the Pirson's hard–soft acids concept. As is known [10–12], as a quantitative characteristics adequate to a metal ion hardness can be taken so called orbital electronegativity of the metal ion which is higher when hardness is also higher. According to the data in [11, 12], this value for the doubly charged ions of 3*d*-elements in gas phase is 13.08 (Cr^{2+}), 13.59 (Mn^{2+}), 14.11 (Fe^{2+}), 14.47 (Co^{2+}), 15.00 (Ni^{2+}), 15.44 (Cu^{2+}) and 15.82 eV (Zn^{2+}). For the VO^{2+} ions there

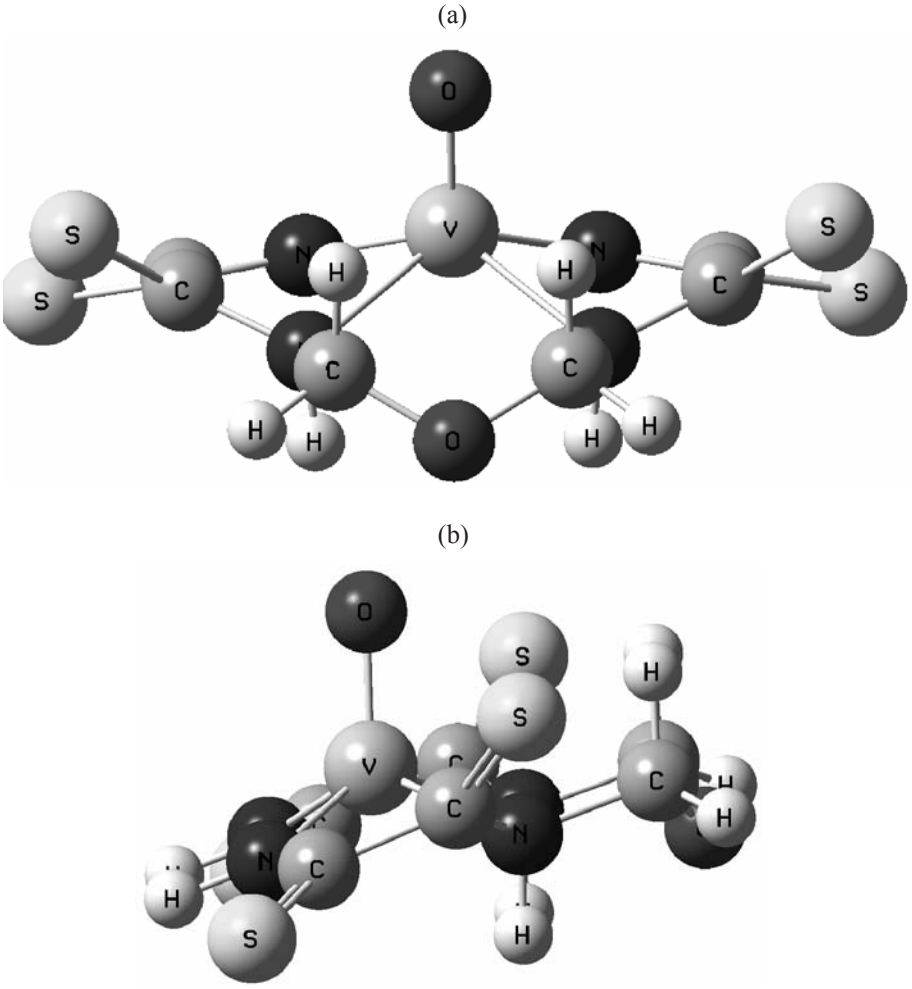
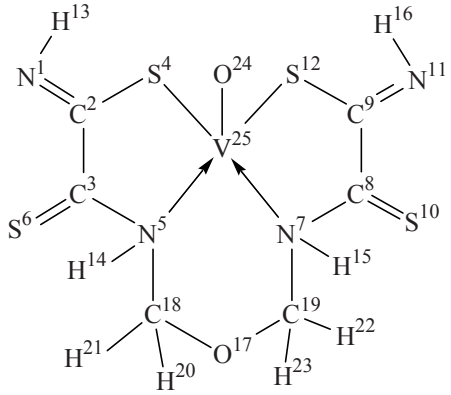


Fig. 2. Steric structure of (VO)(IV) complex of **II** type: (a) front view and (b) side view.

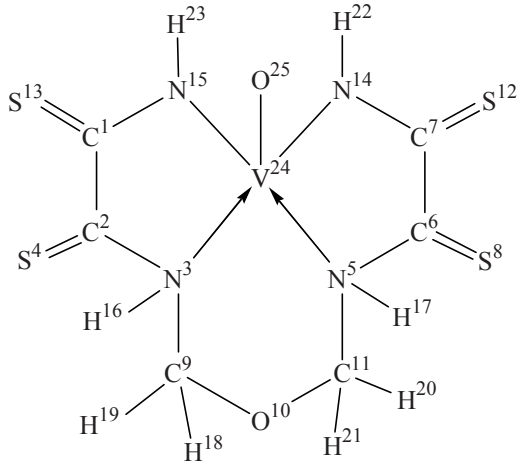
Table 1. Calculated geometric parameters of (VO)(IV) complex of **I** type



Atom no.	Chemical element	Cartesian coordinates of atom, pm			Bond lengths, pm			
		x	*y*	*z*				
1	N	–420.60	133.60	19.79	*d*(1,2)	130.97	*d*(8,9)	149.78
2	C	–297.08	94.75	0.15	*d*(1,13)	102.28	*d*(8,10)	162.43
3	C	–276.01	–44.81	14.99	*d*(2,3)	141.92	*d*(9,11)	127.45
4	S	–161.00	198.64	–43.67	*d*(2,4)	176.72	*d*(9,12)	178.68
5	N	–142.06	–99.38	4.28	*d*(3,5)	145.03	*d*(11,16)	102.52
6	S	–415.57	–142.43	33.50	*d*(3,6)	171.31	*d*(12,25)	237.59
7	N	148.43	–103.15	8.06	*d*(4,25)	238.89	*d*(17,18)	140.54
8	C	282.16	–49.22	24.98	*d*(5,14)	102.56	*d*(17,19)	139.90
9	C	306.05	73.94	–56.85	*d*(5,18)	150.51	*d*(18,20)	109.17
10	S	386.92	–116.03	129.59	*d*(5,25)	218.93	*d*(18,21)	109.63
11	N	417.17	85.96	–118.10	*d*(7,8)	145.19	*d*(19,22)	109.57
12	S	169.57	189.17	–52.49	*d*(7,15)	102.40	*d*(19,23)	109.25
13	H	–441.69	228.89	–10.81	*d*(7,19)	151.05	*d*(24,25)	156.65
14	H	–132.22	–173.77	74.20	*d*(7,25)	219.75		
15	H	139.13	–179.70	75.43				
16	H	421.19	175.17	–168.46				
17	O	4.26	–236.64	–125.37				
18	C	–115.85	–163.76	–129.22				
19	C	122.95	–162.67	–128.42				
20	H	–195.17	–235.38	–151.52				
21	H	–114.11	–84.13	–204.55				
22	H	120.23	–81.08	–201.52				
23	H	203.06	–232.91	–152.58				
24	O	5.15	63.71	210.27				
25	V	3.99	56.01	53.82				

are no such data, but judging from the above variations in orbital electronegativity of M^{2+} ions its orbital electronegativity in gas phase should be either below 13.0 eV, or at least should fall to the range of other M^{2+} ions. Anyway, these values of orbital electronegativity in gas phase are typical of hard Pirson's acids. In correspondence with the general Pirson's rule [10] in the case when ligand possess donor atom with either relatively low or high electronegativity (just like the atoms S and N), at the complex formation this ligand should coordinating with hard acids through the donor atoms with high electronegativity. Therefore it is

Table 2. Calculated geometric parameters of structure of the complex (VO)(IV) of **II** type



Atom no.	Chemical element	Cartesian coordinates of atom, pm			Bond lengths, pm			
		x	*y*	*z*				
1	C	–273.57	–117.98	–13.28	*d*(1,2)	151.23	*d*(7,14)	134.97
2	C	–271.65	32.95	–4.03	*d*(1,13)	166.21	*d*(9,10)	140.81
3	N	–147.18	82.02	–60.66	*d*(1,15)	134.97	*d*(9,18)	109.16
4	S	–381.17	129.77	66.78	*d*(2,3)	145.28	*d*(9,19)	109.38
5	N	147.19	82.03	–60.68	*d*(2,4)	162.43	*d*(10,11)	140.81
6	C	271.65	32.95	–4.04	*d*(3,9)	148.82	*d*(11,20)	109.38
7	C	273.57	–117.98	–13.31	*d*(3,16)	102.64	*d*(11,21)	109.16
8	S	381.17	129.76	66.80	*d*(5,6)	145.28	*d*(14,22)	101.89
9	C	–119.83	228.31	–59.94	*d*(5,11)	148.83	*d*(14,24)	199.22
10	O	–0.01	252.74	–129.74	*d*(5,17)	102.64	*d*(15,23)	101.89
11	C	119.84	228.32	–59.99	*d*(6,7)	151.23	*d*(15,24)	199.21
12	S	413.77	–201.26	–45.46	*d*(6,8)	162.43	*d*(24,25)	157.19
13	S	–413.76	–201.27	–45.48	*d*(7,12)	166.20		
14	N	149.10	–167.63	2.72				
15	N	–149.10	–167.64	2.78				
16	H	–140.14	47.87	–157.20				
17	H	140.14	47.85	–157.21				
18	H	–198.91	282.17	–112.49				
19	H	–115.32	261.25	44.26				
20	H	115.39	261.29	44.21				
21	H	198.90	282.15	–112.59				
22	H	147.41	–269.48	0.11				
23	H	–147.42	–269.48	0.18				
24	V	0.00	–42.01	43.67				
25	O	0.00	8.49	192.53				

expectable that complex **II** with its chelate node VN_4 should have lower energy than complex **I** with its VN_2S_2 chelate node. Such conclusion, as is not difficult to see, is completely consistent with the results of our calculations. However, calculations of free Gibbs energy ΔG^0_{298} for both the reactions (1) and (2), give positive values (1394.46 and 1027.44 kJ, respectively); hence, under standard conditions both

these reactions are forbidden. But is absolutely obvious that they can not proceed also at higher temperature because (like the case of any other reaction of template synthesis) the total entropy of the system decreases [7, 8] (that is, $\Delta S^0_{298} < 0$). From this follows that template process in the system V(IV)–dithiooxamide–formaldehyde in gas phase theoretically should not occur at all [at least in the form of reactions (1) and (2)], although at least one of the formed complexes, namely **II**, is capable of existing independently.

As to the possibility of prognosis of proceeding certain reaction (1) or (2) in aqueous solution or in solid phase, the situation is much more complicated

The values of orbital electronegativity for the doubly charged ions of 3*d* elements in aqueous solution according to [11, 12] are 0.91 (Cr^{2+}), 0.66 (Mn^{2+}), 0.69 (Fe^{2+}), 0.52 (Co^{2+}), 0.29 (Ni^{2+}), –0.55 (Cu^{2+}) and –1.02 eV (Zn^{2+}). As seen, these values are actually in opposite order as compared with gas phase. The values of orbital electronegativity of Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} are typical for the acids of moderate strength, while Cu^{2+} and Zn^{2+} are soft Pearson's acids [12]. Again there is no related data for VO^{2+}, but undoubtedly this compound belongs to the group of hard Pearson's acids [11, 12]. On the other hand, by its hardness VO^{2+} should be below Co^{3+}. Noteworthy that according to [13] the gelatin-immobilized Co(II) hexacyanoferrate $K[CoFe(CN)_6]$ also enters to the template reaction with dithiooxamide and formaldehyde, affording therewith the Co(III) complex just with (NNSS)-coordination of the helant donor centers to the complex forming moiety. In this connection there are all reasons to suggest that at the complex formation by VO^{2+} with dithiooxamide and formaldehyde under specific conditions of dioxovanadium(IV) hexacyanoferrat(II) gelatin-immobilized matrix is more probable formation of the complex with structure **I**. This conclusion however is not consistent with the results of quantum-chemical calculation of energy of complexes **I** and **II**, but remember that the calculation relates to gas phase reactions, while in the case of condensed state of reaction medium (liquid phase or solid phase) the relation of these energy values can change considerably or even inverted.

According to the data of quantum-chemical calculation by the same B3LYP method with 6-31G(d) basis set [14], the values of ΔG^0_{298} for the gas phase reactions like reaction (1) but with hexacyanoferrates(II) with other M^{2+} cations are 1343.84 (Mn^{2+}), 1120.66 (Co^{2+}), 1060.67 (Ni^{2+}) and 668.00 (Cu^{2+}) kJ. For $VO^{2+}\Delta G^0_{298}$, as noted above, equals 1394.46 kJ, hence, a bit higher than ΔG^0_{298} value for the Mn^{2+} complex. Note in this connection that despite the themodynamic prohibition for proceeding each of these reactions in gas phase, in the metal(II)hexacyanoferrate(II) gelatin-immobilized matrix it nevertheless proceeds, at least this is observed in the cases of Co^{2+}, Ni^{2+} and Cu^{2+} [1–6]. Therefore there are reasons to expect that reaction (1) in dioxavanadium(IV) hexacyanoferrat(II) gelatin-immobilized matrixt can be realized.

Method of Calculation

For the quantum-chemical calculations was used three-parametric hybrid method of density functional B3LYP (unrestricted by spin) with standard basis set 6-31G(d) [15]. The calculations were carried out using Gaussian 98 package [16]. Correspondence of the found stationary point in each case was evidenced by calculation of Hessian (all terms in the matrix of second derivatives are positive).

All the quantum-chemical calculations were carried out in the Supercomputer Center of Kazan Scientific Center of Russian Academy of Sciences.

ACKNOWLEDGMENTS

The authors are deeply grateful to Russian Foundation for Basic research for the financial support of preparation of this article (grant no. 06-03-32003).

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