Kinetics and Catalysis, Vol. 42, No. 5, 2001, pp. 653–656. Translated from Kinetika i Kataliz, Vol. 42, No. 5, 2001, pp. 720–723.
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On the Nuclearity of the Vanadium(II)–Pyrocatechol Complex Active in the Reaction of Molecular Nitrogen Reduction

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Received August 22, 2000

Abstract—A detailed analysis of the previously obtained EPR spectra of the V(II)–pyrocatechol complex active in the reduction reaction of molecular nitrogen was performed. On the basis of structural data for related systems, a previous interpretation based on the complete disappearance of exchange interactions was revised. The hyperfine structure of the EPR spectrum of the test complex was explained as a consequence of strong exchange interactions, which effectively withdraw a portion of V atoms. A conclusion on the tetranuclear character of the active complex was made.

INTRODUCTION

The catecholate complexes of V(II) have the unique property of reducing nitrogen to ammonia in homogeneous protic media (water or alcohol) [1, 2]. This process is highly efficient because of the polynuclear nature of the active center [2], which facilitates the many-electron reduction of nitrogen. However, the number of vanadium ions in a polynuclear active center remained unknown until recently, and conclusions on its composition are contradictory.

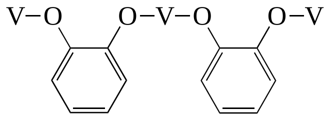
In early works [3] devoted to the mechanism of nitrogen fixation by the catecholate complexes of vanadium, the following reaction scheme with the participation of a tetranuclear complex of V(II) (henceforth, all ligands other than nitrogen in vanadium complexes are omitted) was suggested:

$$\begin{gathered} V_4 + N_2 \rightleftarrows V_4N_2, \\ V_4N_2 + V_4 + 8H^+ \longrightarrow 8V(III) + 2NH_3 + H_2, \end{gathered} \qquad \text{(I)}$$

This reaction scheme adequately explained the ratio between the ammonia and hydrogen formed at nitrogen-saturation pressures. The kinetics of hydrogen formation in the absence of nitrogen is described by a one-half order with respect to the vanadium complex. This can also be well explained on the assumption that hydrogen is formed on binuclear V(II) complexes, which are in equilibrium with tetranuclear complexes (with tetranuclear complexes predominant):

$$\begin{gathered} V_4 \rightleftarrows 2V_2, \\ V_2 + 2H^+ \longrightarrow 2V(III) + H_2. \end{gathered} \qquad \text{(II)}$$

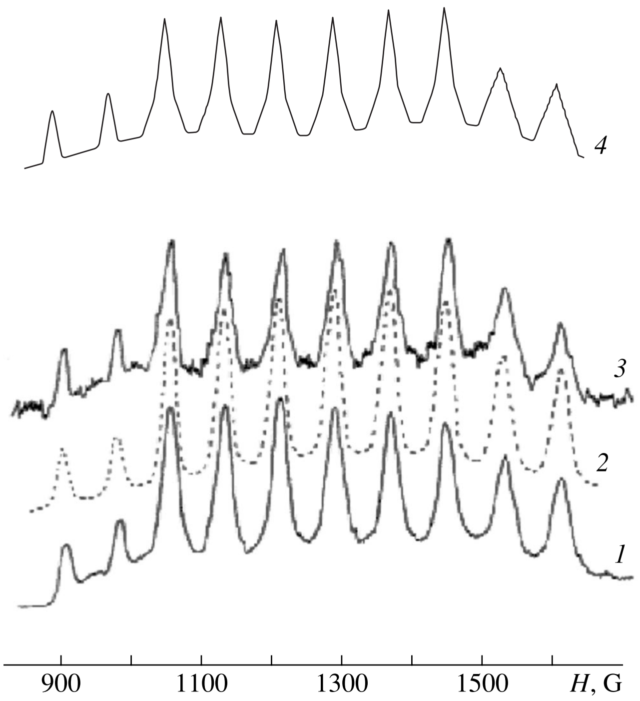
In the subsequent study [4] of the reaction mixture by EPR spectroscopy, a signal of ten lines (see the figure) was detected in the region of a *g*-factor of 5.3. The signal intensity correlated well with the apparent rate constant of nitrogen reduction. On this basis, a conclusion was drawn that the complex responsible for the EPR signal activates and reduces N_2. This signal was interpreted previously [4] in terms of a trinuclear V(II) complex with two types of vanadium atoms with no exchange interactions,



(III)

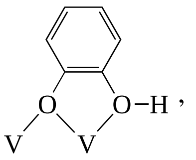
In this case, with a considerable zero-field splitting, the decuplet of lines could be described by the superposition of two octets of Gaussian lines (the nuclear spin of V is equal to 7/2) with weights of 1 : 2. However, as can be seen in the figure, only the peak intensities approximately satisfy the theoretical ratio 1 : 3 : 2, whereas the integral intensities do not satisfy this ratio because of a detectable difference of two low-field line widths from the remaining line widths. Therefore, it is evident that this interpretation needs to be revised. Moreover, the introduction of the trinuclear active complex resulted in a more complicated mechanism of nitrogen reduction because of the incorporation of a step of formation of an intermediate tetranuclear complex of nitrogen from the trinuclear complexes [4]. Another argument against the trinuclear complex is the absence of a plausible explanation for the above one-half order of reaction with respect to the vanadium complex in the description of the kinetics of hydrogen liberation in the absence of nitrogen.

A study of the modified vanadium–pyrocatechol system (with di-*tert*-butylpyrocatechol) made it possible to isolate a tetranuclear mixed-valence V(II)–V(III) complex and to determine its molecular structure [5]. The related structures of vanadium complexes, which were studied in [6–9], exhibited various types of coordination of a catecholate ligand or another bidentate ligand. However, none of these ligands acts as a bridge, as is the case in (III), which could explain the absence



Low-field component of the EPR spectra of vanadium complexes measured under different conditions: (*1*) $T = 77$ K; modulation frequency of 100 kHz [4]; (*3*) $T = 1.5$ K; modulation frequency of 80 Hz [4]. The spectra simulated based on (*2*) trinuclear [4] and (*4*) tetranuclear complexes.

of the magnetic interaction between vanadium atoms. The studied structures exhibit bridge coordination of a catecholate ligand like



which is responsible for the direct exchange between vanadium atoms through a bridging oxygen atom. Thus, the above structural data are inconsistent with the hypothesis on the disappearance of exchange interactions.

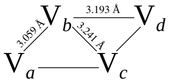
A detailed analysis preformed recently demonstrated that the kinetic data on the four-electron reduction of nitrogen by pyrocatechol complexes of vanadium(II) to a hydrazine derivative can be adequately described only under the assumption of the presence of a tetranuclear active complex [10].

As mentioned above, vanadium(II) complexes with pyrocatechol and its analogs remain the only known family of complexes capable of reducing N_2 in homogeneous protic media (water or methanol). Thus, the problem of active species reacting with N_2 is of fundamental importance. In the context of new data and ideas, we returned to the problem of nuclearity of complexes active toward nitrogen in the V–pyrocatechol system.

From the standpoint of interpretation of EPR spectra, transition metal clusters with exchange interactions are a rather complicated system [11]. In the absence of detailed structural information, the spectra can be interpreted only qualitatively. In this respect, the well-studied case [12] of a heterometallic octanuclear cluster with a spin of 3/2, which forms a nucleus of Fe–Mo cofactor, is of interest. Experimental data suggest low localization of unpaired electrons and, hence, a low hyperfine interaction constant at the Mo(IV) center despite its local high-spin state in an octahedral ligand environment. This circumstance demonstrates that antiferromagnetic interactions in a polynuclear complex with nonequivalent centers can significantly affect the hyperfine interaction constants of individual paramagnetic atoms.

Let us consider the interpretation of EPR spectra of an active V(II)–pyrocatechol complex in terms of the initial idea of a tetranuclear complex.

As the prototype of an intermediate active complex,[1] we decided on the centrosymmetrical mixed-valence complex $V_2^{II}V_2^{III}$ of much the same composition and with rhomboidal arrangement of its atoms:



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this complex was studied in [5]. Generally, it is clear that exchange interactions between equivalent V_b and V_c atoms and nonequivalent V_a, V_b and V_a, V_c atoms are different. Moreover, exchange interaction between spatially spaced V_a and V_d atoms is insignificant. In this situation with strong antiferromagnetic V_b–V_c interactions, the EPR spectrum of this tetranuclear complex in a certain conformation will exhibit only eight lines. Generally speaking, several conformations or structural isomers of this kind can occur, which result from different mutual locations of bidentate pyrocatechol ligands at available coordination sites differing little in energy. As a result, at a corresponding similarity of hyperfine interaction constants and *g*-factors for two coexisting conformers of a tetranuclear complex, the superposition of two octets in the observed EPR spectrum can be unresolved and contain 10 lines. On the one hand, this circumstance can explain the observed temperature independence of the ratio between the components of an EPR spectrum of a frozen sample. On the other hand, an arbitrary ratio between the intensities of octets can be used. The above consideration demonstrates that

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[1] Note that a tetranuclear complex of nitrogen with rhomboidal arrangement of its coordinating metal centers is known for Sm(II) [13]. Because the f^6 and f^5d configurations are energetically similar, this complex can be considered an analog of the complex of a nitrogen molecule with four atoms of transition metals, in which the four-electron reduction of this molecule takes place.

the EPR spectrum of a polynuclear complex can contain a smaller number of lines not only due to a decrease in all exchange interactions in the system but also due to the opposite situation, when signals from a portion of the centers disappear because of strong antiferromagnetic interactions between them.

Based on data [14] on the relation between the sign of exchange interactions and the symmetry of overlapping of magnetic orbitals, let us analyze the differences in the exchange interactions between V atoms. For V_b and V_c atoms in the central part of the complex, the overlapping of singly occupied *d* orbitals is allowed by symmetry rules because these atoms are equivalent. In the case of interactions between nonequivalent V_a, V_b and V_a, V_c atoms, any overlap symmetry can be absent. Thus, bearing in mind that the limiting case of zero overlapping corresponds to ferromagnetic interaction [14], we can conclude that the assumption that the energy of exchange interactions between nonequivalent V atoms is lower than that for equivalent V atoms is well substantiated. Note that in a tetranuclear Fe(II) complex, which is structurally similar to the complex $V_2^{II}V_2^{III}$ both in its type of metal framework and number and arrangement of μ_2- and μ_3-bridging groups, the above magnetic interactions differ by more than one order of magnitude. In this case, the interactions between nonequivalent centers are weak and ferromagnetic and the interaction between spatially separated centers is absent [15]. It is difficult to evaluate the magnetic properties of the complex of interest in more detail because it is well known that the exchange integral is very sensitive to both the distance between the magnetic centers for direct exchange and the M–X–M angle for indirect exchange through the ligand X. In this case, the pair of V_b and V_c atoms also stands out because the exchange occurs through the bridging atoms of μ_3-bridge groups only in this pair.

Thus, it is reasonable to believe that the V_b–V_c exchange interactions are considerable. As a result of these interactions, the active V(II) complex can be considered magnetically as a set of two almost noninteracting centers V_a and V_d. On the assumption that the tetranuclear V complex has two conformations, the decuplet observed in the EPR spectrum can be interpreted by the superposition of two octets. Either of the octets can be ascribed to one of the conformers of the tetranuclear complex if we assume that the hyperfine interaction constants (A) are similar for both of the conformers and the difference between the *g*-factors randomly corresponds to the value of A.[2] The assumption that the tetranuclear V complex has two conformations is reasonable because of the loosened character of the complex active toward nitrogen, taking into account that this complex is converted into a mononuclear V(II) complex as the pH of the medium is increased [4].

The electron coupling of V_a and the equivalent center V_d with the zero-spin V_b–V_c dimeric fragment should be taken into account in detailed consideration of the EPR spectra. Then, each of the octet components is really a set of 15 lines because of the low hyperfine splitting on the two equivalent nuclei V_b and V_c. On this basis, a theoretical EPR spectrum in the low-field region was constructed for the tetranuclear complex with strong antiferromagnetic interaction between atoms V_b and V_c taking into account the nonequidistance of hyperfine structure components. The positions of line centers for individual conformers were calculated by the Zeeman splitting equation,

$$\Delta E = g\beta H + Am_I + \frac{A^2}{2g\beta H}[I(I+1) + m_I^2],$$

where $I = 7/2$ is the nuclear spin of vanadium, m_I takes values from –1 to +1, and β is the Bohr magneton. The ground-state splitting $A = 84$ G was taken to be equal for both of the conformers at different *g*-factors. The shape of each line was described taking into account secondary splitting on V_b and V_c nuclei with the hyperfine coupling constants A_1 and A_2 equal to 1.7 and 4 G, respectively, depending on the conformation type. In both cases, individual components were described by Gaussian lines with the half-width $\Delta = 4.4$ G. The fine structure of the spectrum cannot appear because of the small values of constants A_1 and A_2 with respect to the width Δ of an individual line. However, the contour of the observed integrated line will reflect the "triangle" intensity ratio 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 7 : 6 : 5 : 4 : 3 : 2 : 1 for two equivalent nuclei with a spin of 7/2. Indeed, this relation fits the contour of lines in EPR spectra better than Gaussian and Lorentzian functions (figure); in specific cases, even characteristic irregularities of the contour can be seen. The figure also demonstrates the spectrum constructed in this manner at a ratio of ~1 : 3 between the integral intensities of octets superimposed on an experimental background line. A comparison of this spectrum with experimental data suggests that it adequately reproduces not only the peak intensities but also the widths and shapes of the observed lines.

Thus, a refined analysis of EPR spectra allowed us to conclude that a tetranuclear V(II) complex is the most probable complex species active toward the reduction of molecular nitrogen in the V(II)–pyrocatechol system.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 96-15-97371.

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[2] The assumptions underlying this interpretation can be experimentally tested by measuring magnetic susceptibilities or EPR spectra in different microwave ranges.

REFERENCES

1. Luneva, N.P., Nikonova, L.A., and Shilov, A.E., *React. Kinet. Catal. Lett.*, 1976, vol. 5, no. 2, p. 149.
2. Shilov, A.E., *Metal Complexes in Biomimetic Chemical Reactions*, New York: CRC, 1997.
3. Luneva, N.P., Nikonova, L.A., and Shilov, A.E., *Kinet. Katal.*, 1980, vol. 21, no. 6, p. 1458.
4. Luneva, N.P., Moravskii, A.P., and Shilov, A.E., *Nuov. J. Chem.*, 1982, vol. 6, no. 3, p. 245.
5. Luneva, N.P., Mironova, S.A., Shilov, A.E., *et al.*, *Angew. Chem.*, 1993, vol. 32, no. 8, p. 32.
6. Bonitzeto, P.J. and Armstrong, W.H., *J. Chem. Soc., Chem. Commun.*, 1999, no. 1, p. 55.
7. Cooper, S.R., Kon, Y.B., and Raymond, K.N., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 10, p. 5092.
8. Luneva, N.P., Mironova, S.A., Lysenko, K.A., and Antipin, Yu.A., *Koord. Khim.*, 1997, vol. 23, no. 12, p. 899.
9. Janes, Z., Sobota, P., Kasprzak, M., and Glowiak, T., *J. Chem. Soc., Chem. Commun.*, 1996, no. 24, p. 2727.
10. Dzhabiev, T.S., Mironova, S.A., and Shilov, A.E., *Kinet. Katal.*, 1999, vol. 40, no. 6, p. 844.
11. Belinskii, B.S. and Tsukerblatt, M.I., *Magnetokhimiya i EPR-spektroskopiya poliyadernykh kompleksov s obmennymi vzaimodeistviyami* (Magnetochemistry and ESR Spectroscopy of Complexes with Exchange Interactions), Chisinau: Shtiintsa, 1983.
12. Munck, E., Rhodes, H., Orme-Johnson, W.H., *et al.*, *Biochim. Biophys. Acta*, 1975, vol. 400, no. 1, p. 32.
13. Dube, T., Conoci, S., Gambarotta, S., Yap, G.P.A., and Vasapollo, G., *Angew. Chem.*, 1999, vol. 38, no. 24, p. 3657.
14. Kahn, O., *Inorg. Chim. Acta*, 1982, vol. 62, no. 1, p. 62.
15. Bel'skii, V.K., Ishchenko, V.M., Bulychev, B.M., *et al.*, *Inorg. Chim. Acta*, 1985, vol. 96, no. 2, p. 123.