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ESR spectra of paramagnetic palladium complexes

G. M. Larin, T. A. Stromnova, and S. T. Orlova*

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279. E-mail: lagema@igic.ac.ru

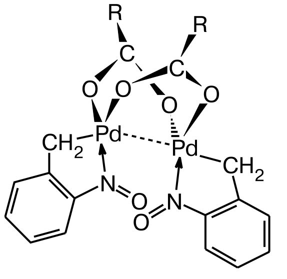
Binuclear nitrosopalladium complexes $Pd_2(\mu\text{-}COOR)_2(\eta^2\text{-}CH_2C_6H_4NO)_2$ (R = Me, CF_3, or Ph) were studied by ESR spectroscopy. Analysis of parameters of ESR spectra of the polycrystalline samples and their toluene solutions suggests partial izomerization of the nitroso ligands to the nitroxide form to result in the oxidation of palladium(II) to palladium(III).

Key words: palladium, nitroso and nitroxide forms, ESR spectroscopy, hyperfine structure.

The chemistry of coordination palladium compounds has been intensely developed during the last three—four decades, because many of these compounds are efficient catalysts for chemical reactions and processes.[1—4]

In the most part of compounds, palladium has the oxidation state 2+ and electronic configuration d^8. If Pd^{II}, by analogy to Ni^{II}, forms compounds with the octahedral or tetrahedral coordination sphere when the highest degenerate orbitals E_g (octahedron) or T (tetrahedron) contain two unpaired electrons, these compounds would possess paramagnetic properties. However, all of the known Pd^{II} compounds are tetracoordinate and planar. For this structure of the coordination sphere, the degeneration of the highest orbitals is eliminated and eight electrons are paired on the four orbitals: d_{xy}, d_{xz}, d_{yz}, and d_{z^2}; the last non-degenerate orbital $d_{x^2-y^2}$ remains unoccupied and, hence, all compounds of Pd^{II} are diamagnetic. Palladium with the oxidation state 1+ and electronic configuration d^9 has one unpaired electron, *i.e.*, it should be in the paramagnetic state. However, Pd^I has a pronounced tendency to form metal—metal bonds due to unpaired electrons and, as a result, these compounds are diamagnetic.[5] Only three works[6—8] are known that describe the preparation of the paramagnetic Pd^I compounds. The palladium compounds with the oxidation state 3+ are very unstable, and only about ten Pd^{III} complexes in solutions have been reported to presently.[9—11] Some of them were also isolated in the solid state.[12,13]

In this work, we used the ESR method to study the binuclear nitrosopalladium complexes $Pd_2(\mu\text{-}COOR)_2(\eta^2\text{-}CH_2C_6H_4NO)_2$ (R = Me (**1a**), CF_3 (**1b**), Ph (**1c**)) in which each palladium atom is bonded to an *o*-nitrosotoluene molecule metallated at the methyl group.



$Pd_2(\mu\text{-}COOR)_2(\eta^2\text{-}CH_2C_6H_4NO)_2$
R = Me (**1a**), CF_3 (**1b**), Ph (**1c**)

Experimental

The synthesis of complexes **1a—c** from *o*-nitrosotoluene *o*-ONC_6H_4Me and carbonylcarboxylate complexes $Pd_4(\mu\text{-}COOR)_4(\mu\text{-}CO)_4$ was described elsewhere.[14,15] The structure of complex **1b** was characterized[14] by X-ray diffraction analysis. The crystals of **1b** are orthorhombic, space group $Pna2_1$. A molecule of **1b** can also be solved in the space group *Pnam*. In this case, the molecule lies on the mirror plane *m* and contains disordered fragments CF_3 and NO and CH_2 groups ($R = 0.061$, $R_w = 0.082$). The Pd—Pd distance is 2.871(1) Å.

ESR spectra of solid polycrystalline powders or solutions in toluene with a low concentration of the compounds under study were recorded on a Radiopan SE/X-2542 radiospectrometer with a working frequency of 9.45 GHz. The spectra of the polycrystalline powders obtained at room temperature and at 77 K were identical. Spectra of solutions in toluene were measured at room temperature. To decrease linewidths in the ESR spectra, argon was passed through the solutions to remove molecular oxygen. The magnetic field was calibrated using a nuclear magnetometer with the use of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as internal field standard.

The experimental spectra (Fig. 1) were processed by computer simulation to the best fit between experimental and theoretical spectra by the error functional minimization

$$R = \Sigma_i(I_i^{\mathrm{exp}} - I_i^{\mathrm{calc}})^2/N, \tag{1}$$

where I_i^{exp} are the experimental intensities of the ESR signal transmitted to the computer memory as an array of points with a constant magnetic field increment *H*; I_i^{calc} are the theoretical intensities at the same *H* values that were calculated as a convolution of derivatives of the Lorentz and Gauss functions centered around the resonance *H* values; *N* is the number of points.

The values of *g* factors, HFS constants from nuclei of the ligand atoms, and resonance linewidths were varied

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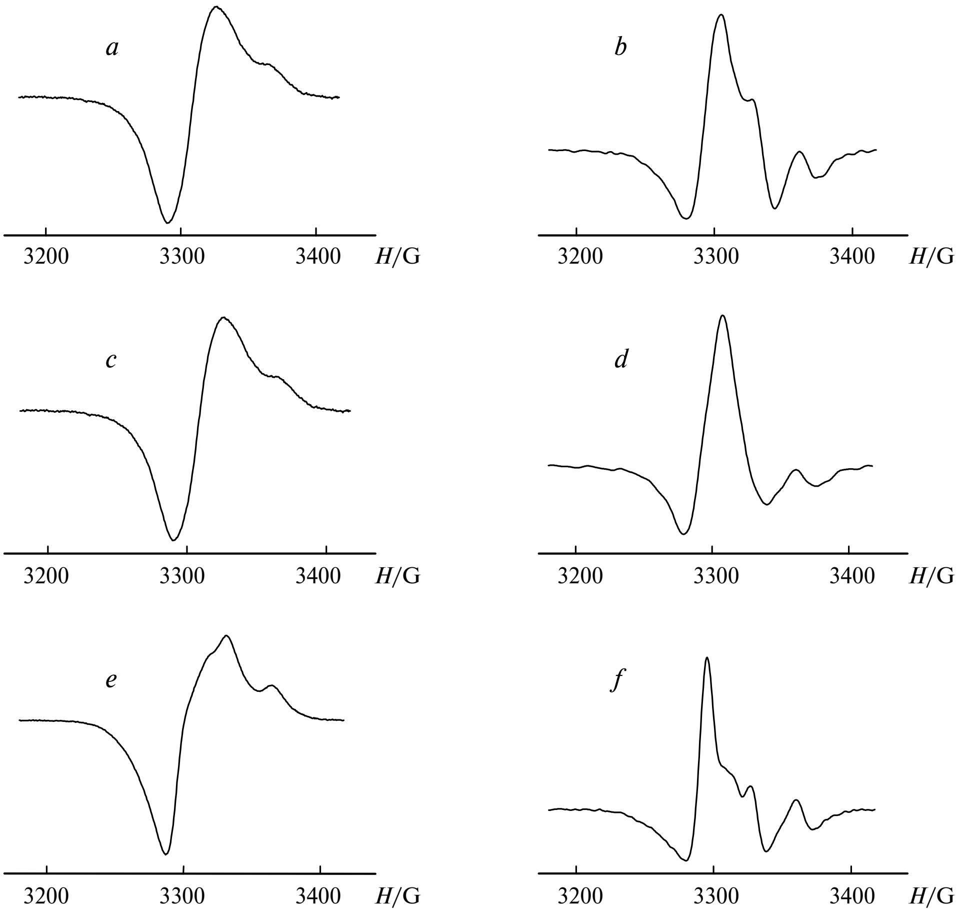


Fig. 1. ESR spectra of complexes **1a** (*a*, *b*), **1b** (*c*, *d*), and **1c** (*e*, *f*) in polycrystalline samples; the first (*a*, *c*, *e*) and second (*b*, *d*, *f*) derivatives of the ESR spectra.

during the minimization. The linewidth was specified by the equation

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2, \qquad (2)$$

where m_I is the projection of the nuclear spin on the external magnetic field direction, and α is the term that takes into account broadening effects, which are the same for all HFS lines. The β coefficient is determined by the product of the *g* tensor and HFS tensor. The γ coefficient is determined by the HFS anisotropy and depends on the correlation time of rotation motion of a paramagnetic particle in liquid. The minimization procedure was stopped at the *R* values when the theoretical spectrum coincided well with the experimental spectrum and further iterations did not change *R* (spectral amplitude was normalized to unity). This usually takes place at $R < 0.003$. Figures 2 and 3 illustrate the achieved degree of agreement.

Results and Discussion

Measurement of magnetic susceptibility of complexes **1a—c** showed that all three compounds are diamagnetic. For this reason, they were not studied in detail for a long time. Since one of the important trends of our studies is the synthesis of coordination compounds of d-metals in unusual oxidation states, we attempted to oxidize or reduce Pd^{II} in compounds of the type of **1**. The rigid structure of the dinuclear polyhedron suggested that palladium can be stabilized in such a coordination environment in an unusual oxidation state. However, before studying redox reactions of compounds **1**, we recorded their ESR spectra. It turned out that intense signals are observed in the spectra of the solid polycrystalline samples, which indicates a great impurity of paramagnetic compounds. To exclude the influence of possible paramagnetic admixtures, we newly synthesized complexes **1** and studied the ESR spectra of all of the starting compounds. These compounds, *viz*., clusters $Pd_4(\mu\text{-COOR})_4(\mu\text{-CO})_4$ and *o*-nitrosotoluene, turned out to be diamagnetic.

The ESR spectra of the solid polycrystalline powders exhibit signals with broad linewidths with the two-axial (**1b**) or three-axial (**1a** and **1c**) anisotropy of *g* factors. The three-axial anisotropy is especially pronounced in the ESR spectra of compounds **1a** and **1c** recorded as the second derivative (see Fig. 1, *b*, *f*). The parameters of the first and second derivatives of the spectra of the solid poly-

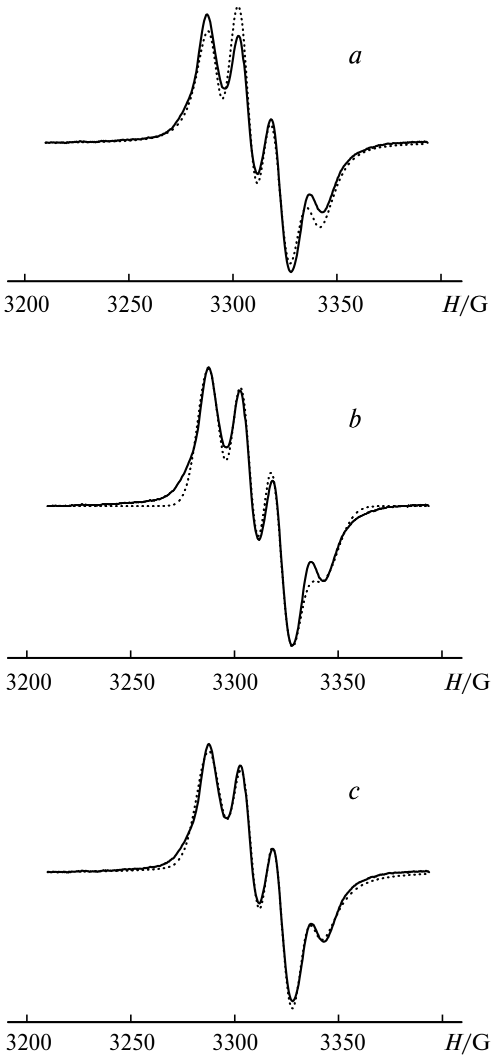


Fig. 2. ESR spectrum of compound **1a** in a toluene solution for splitting 1 : 3 : 3 : 1 (*a*), (1 : 1 : 1)×(1 : 1) (*b*), and (1 : 1 : 1)×(1 : 1 : 1) (*c*). Solid lines are experiment, and dotted lines are calculation.

crystalline powders of compounds **1a,b** are given in Table 1. The parameters of the ESR spectra of the solid crystalline samples show unambiguously that the spectra are caused by coordination compounds of a paramagnetic d-metal. This conclusion can easily be substantiated by the following arguments. First, the ESR spectra of polycrystalline samples of organic radicals in the X range (~10 GHz) never exhibit the *g* factor anisotropy, because it is ~0.001.[16] Second, polycrystalline samples of organic radicals never have ESR spectra with linewidths exceeding ~10 G. For instance, the width of the singlet signal from the polycrystalline DPPH radical is only 1.9 G, and the asymmetry value of the singlet in a range of 9.45 GHz (3.2 cm) is negligible: only 2.8%. This indicates that at a working radiospectrometer wavelength of 3.2 cm the *g* factor anisotropy of the radicals is not virtually observed.

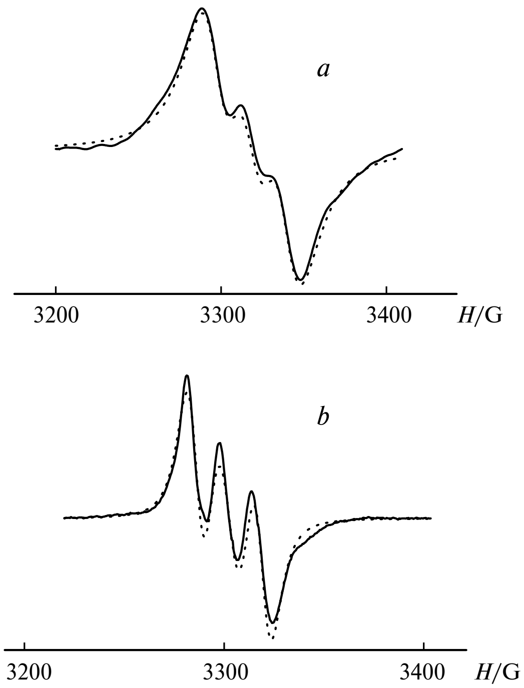


Fig. 3. ESR spectra of compounds **1b** (*a*) and **1c** (*b*) in toluene solutions. Solid lines are experiment, and dotted lines are calculation.

For the polycrystalline samples of **1a—c**, the ESR spectra have the two- and three-axial anisotropy of *g* factors, and the *g* factor values are close to those for the earlier studied Pd^{III} and Pt^{III} compounds (see Table 1). In addition, in the first derivative of the ESR spectra, the minimum width is 25 G (**1b**) and the maximum width is 44.6 G (**1c**), which exceeds considerably the linewidths in the ESR spectra of organic radicals. Thus, the ESR spectra presented in Fig. 1 are caused by paramagnetic metal ions.

Table 1. Parameters of the ESR spectra for polycrystalline samples of the palladium nitroso complexes[a]

Compound	g_x±0.001	g_y±0.001	g_z±0.001	ΔH_x/G
1a	2.029	—	1.985	40.0
	(2.029)	(2.006)	(1.985)	(25.0)
1b	2.029	—	1.985	36.3
	(2.029)	—	(1.984)	—
1c	2.031	—	1.984	44.6
	(2.031)	(2.010)	(1.984)	(30.3)
$[Pd(S_2C_2Ph_2)]^{2+}$	2.055	2.044	1.961	—[b]
$[Pt(S_2C_2Ph_2)]^{2+}$	2.171	2.068	1.849	—[c]
Pt^{3+} in YAl garnets	2.424	2.361	1.962	—[d]

[a] The data for the spectra with the first (second) derivative of the lineshape are given.

[b] See Ref. 12.

[c] See Ref. 17.

[d] See Ref. 18.

Table 2. Parameters of the ESR spectra for compounds **1** in toluene solutions

Compound	Type of splitting	g±0.001	a±0.2	α±0.2	β±0.2	γ±0.2	Error (%)
			G				
1a	(1 : 3 : 3 : 1)	2.013	a_H = 15.1	11.2	−0.7	−0.6	4.4
	(1 : 1 : 1)×(1 : 1)	2.013	a_H = 13.9,	9.3	−6.1	8.1	3.7
			a_N = 14.3	7.9	0.2	1.5	—
	(1 : 1 : 1)×(1 : 1 : 1)	1) 2.017,	$a_N{}^1$ = 13.9	11.8	0.4	2.0	1.4
		2) 2.008	$a_N{}^2$ = 15.0	12.2	1.4	1.5	—
1b	(1 : 1 : 1)	2.015	a_N = 12.9	11.4	0.5	0.7	2.5
1c	(1 : 1 : 1)	2.007	a_N = 15.7	10.8	0.2	0.7	3.3

To reveal the nature of formation of d-metal ions in the paramagnetic state, we studied ESR spectra of solutions of **1a—c** in toluene. All compounds **1** in solutions give ESR spectra consisting of several lines. The spectrum of compound **1a** (see Fig. 2) is a quartet, which can be attributed, most probably, to an additional HFS (AHFS) from three equivalent hydrogen atoms of the chelating ligands (spectrum 1 : 3 : 3 : 1). However, it is difficult to find three equivalent hydrogen atoms in structure **1**. In addition, the theoretical spectra 1 : 3 : 3 : 1 plotted by the procedure of error functional minimization (see Eq. (1)) of the theoretical spectrum from the experimental one contain rather high error (Table 2). The experimental and theoretical spectra for the first variant (see Fig. 2, *a*) differ strongly.

This spectrum can also be interpreted as the splitting of a triplet with the 1 : 1 : 1 ratio into the 1 : 1 doublet (see Fig. 2, *b*)[19]. The triplet is referred to the nitrogen atom, and the doublet can be attributed, most likely, to one of the hydrogen atoms of the metallated methyl group of the nitroso ligand. However, it remains unclear why the hydrogen atoms of the metallated methyl group of the nitroso ligand are nonequivalent. At the same time, the spectrum of compound **1a** can be assigned to two compounds with different conformational structures with the HFS from one of the two nitrogen atoms, which are nonequivalent by the geometric arrangement in two conformers (see Fig. 2, *c*). The existence of two conformers is seen from their electronic structures, which causes different *g* factors. For instance, in the copper(II) compounds, insignificant differences in the structure of the coordination sphere and arrangement of the equivalently remote substituents in the chelating ligands result in considerable differences in parameters of the ESR spectra.[20] As mentioned above, compound **1b** can be assigned to the space group *Pnam* even according to the X-ray diffraction data. In this case, the molecule lies in the mirror plane *m* and contains disordered fragments CF_3 and NO and CH_2 groups, *i.e.*, the compound contains geometrically nonequivalent conformer molecules. Perhaps, the same is observed for compound **1a**. Since the error in the theoretical calculation of the spectra is lower in the second case, the latter variant seems more realistic.

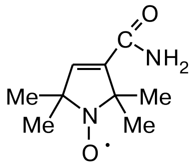
The spectrum of a solution of compound **1b** without oxygen exhibits a poorly resolved triplet (see Fig. 3, *a*). This spectrum is well described by a triplet with the intensity ratio 1 : 1 : 1, which can be attributed only to the HFS from one of the nitrogen atoms of the ligands.

The spectrum of a solution of compound **1c** contains a well resolved triplet from one of the nitrogen atoms of the ligand (see Fig. 3, *b*). The insufficient coincidence of the theoretical and experimental spectra indicates that the lines of the triplet in the experimental spectrum also have an unresolved HFS from other atoms of the ligands.

The parameters of the ESR spectra of the studied binuclear nitrosopalladium complexes in solutions are given in Table 2. The *g* factors are much higher than those of the free radicals and similar to the *g* factors of some Pd^{III} complexes. For example, the *g* factor in the spectra of the Pd^{III} complexes with dithiolates is 2.022 [21] and 2.023,[22] and it is 2.003—2.008 in the organic radicals.[16,23] In addition, for free radicals the linewidth is several G. For instance, the linewidth (ΔH) values in the ESR spectra of a DPPH radical in different solvents are given below (ν = 9.40 GHz).[16]

Solvent	Pyridine	Benzene	Toluene	Chloroform	Carbon disulfide
ΔH/G	5.0	4.7	2.6	2.0	1.5

In the nitroxyl radical 2,2,5,5-tetramethyl-3-carbamoyl-2,5-dihydro-1*H*-pyrrole-*N*-oxyl, the linewidth is 1.5 G in solutions containing no molecular oxygen and increases to 2.5 G in solutions saturated with paramagnetic molecular oxygen.[24] As can be seen from the data in Table 2, the linewidth in the ESR spectra of compounds **1a—c** exceeds 8 G.

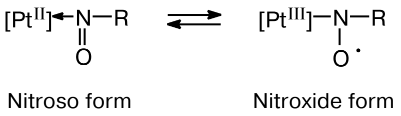


The nature of substituent R in the carboxylate groups of the complexes under study was found to affect the a_N value: a_N decreases from 15.6 to 12.2 G with an increase in the electron-acceptor properties in the series of substituents Ph ≈ Me < CF_3 (see Table 2). The strong difference between the ESR spectra of the three compounds indicates a considerable influence of the nature of the coordinated carboxylate group on the spin density distribution of an unpaired electron over molecules, which can occur only through the palladium atom. Thus, all the above data indicate that paramagnetism is caused precisely by the palladium(III) atoms in the compounds under study. The appearance of HFS in the ESR spectra points to the interaction of an unpaired electron with an element, whose nuclear spin differs from 0, for example, with the nitrogen atom ($I_N = 1$). The computer reconstruction of the spectrum of **1b** shows that this spectrum is well described only with allowance for the AHFS from one nitrogen atom, *i.e.*, it can be said that an electron interacts with the palladium atom and also with the nitrogen atom. The AHFS constants from the nitrogen and hydrogen atoms are characteristic of chelating complexes of d-elements.

However, complexes **1** possess diamagnetic properties (according to the magnetic susceptibility data). It can be assumed that only a small part of molecules of complexes **1** exist in the form that results in the appearance of paramagnetism.

It is known[25] that in transition metal complexes the nitrosoarene ligand can isomerize to the nitroxide anion, which, in turn, increases the formal oxidation state of the metal (Scheme 1).

Scheme 1

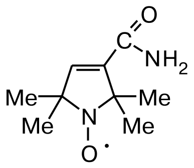


All the above-listed experimental facts satisfy well this hypothesis. Probably, a small part of molecules of **1** isomerize to form the nitroxide form (Scheme 2).

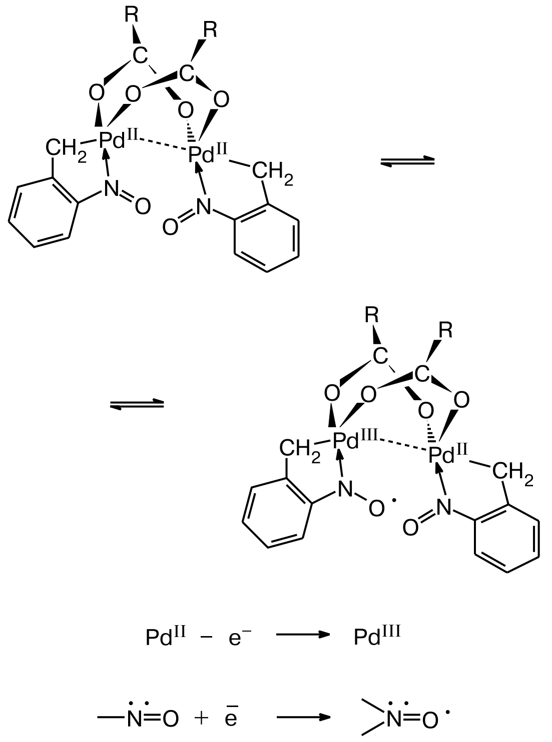
The HFS from one nitrogen atom indicates that the redox reaction occurs between one nitroso group and one Pd^{II} atom

$$Pd^{II} - e^- \rightarrow Pd^{III},$$

The reaction affords Pd^{III} with the electronic configuration d^7, the compound becomes paramagnetic, and a paramagnetic nitroxyl radical is generated. However, this radical is not observed in the ESR spectra. Therefore, we can assume that the radical becomes diamagnetic due to some interactions. Nitroxyl radicals are very reactive and can be stable only if the $\rangle\ddot{N}{=}O^{\bullet}$ group is well sterically protected, as, *e.g.*, in the nitroxyl radical 2,2,5,5-tetramethyl-3-carbomoyl-2,5-dihydro-1*H*-pyrrole-*N*-oxyl in which four Me groups in the *ortho*-position sterically protect the nitro group from other radicals (see monograph[23]). In addition, if the paramagnetic Pd^{III} with one unpaired electron and the nitroxyl group also with one unpaired electron are retained in the dimer of the nitrosopalladium complex, such strong spin-spin interactions through the nitrogen atom would appear between them that the total spin of the complex would be equal to unity ($S = 1$) and the ESR spectra would belong to the triplet spin state. In our case, all the ESR spectra are detected from compounds with the electron spin $S = 1/2$ and are caused by complexes in which an unpaired electron lies on the orbitals of the metal.



Scheme 2



Thus, we observed the ESR spectra of the Pd^{III} complexes formed due to the intramolecular electron transfer in the nitrosopalladium(II) complexes.

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