# EFFECT OF ADDUCT FORMATION AND SOLVATION ON INTRAMOLECULAR SPIN EXCHANGE IN A SPIN-LABELED NICKEL(II) $\alpha$ -DIOXIMATE

M. V. Evstiferov, N. G. Vanifatova,O. M. Petrukhin, A. I. Kokorin,V. A. Reznikov, and L. B. Volodarskii

UDC 541.67:543.422.27:541.49: 547.781.1:546.74

Intramolecular spin exchange in complexes of metals with two molecules of spin-labeled reagent depends mainly on the electronic and spin state of the central atom, the degree of covalency in the metal-donor atom bond, and the spatial organization of the metal complex [1, 2]. The exchange energy can change upon formation in solution of either adducts of the spin-labeled complexes with organic solvent molecules or electron donor-acceptor complexes (EDA-complexes). The exchange integral (J) in inert nonsolvating solvents can be considered to depend only on the nature of the chemical bonds and electronic state of the bridge be-

tween >N=0 groups of the nitroxyl ligands. The MOs of the central atom undergo strong perturbations upon formation of EDA-complexes which can lead to a change of J value.

In this work, the effect of the Ni(II) ion spin state and the character of the metalligand bond on the exchange energy upon adduct formation and solvation is studied for the coordinatively unsaturated Ni(II) complex with 3,4-dioximino-2,2,5-trimethyl-5-phenylpyrrolidine-1-oxyl (NiL<sub>2</sub>).

#### EXPERIMENTAL

3,4-Dioximino-2,2,5-trimethyl-5-phenylpyrrolidine-1-oxyl (HL) (III) was synthesized according to a known route



<u>3-Oxo-4-oximino-2,2,5-trimethyl-5-phenylpyrrolidine-1-oxyl (II)</u>. A solution containing 1 g (I) [3], 1 g MeONa, and 1.2 ml AmONO in 40 ml MeOH was held at 20°C for 12 h and evaporated. The residue was dissolved in 10 ml water, washed three times with 15 ml ether, neutralized with 5% HCl, and extracted three times with 20 ml CHCl<sub>3</sub>. The chloroform extract was dried over MgSO<sub>4</sub> and evaporated. (II) was separated chromatographically on a column filled with silica gel (eluent was a mixture of CHCl<sub>3</sub>:MeOH, 30:1). Yield 1.1 g (97%). Found: C 63.0; H 6.0; and N 11.4%.  $C_{12}H_{15}N_2O_3$ . Calculated: C 63.2; H 6.1; and N 11.3%. IR spectrum (cm<sup>-1</sup>): 1760 (C=O) and 1630 (C=N). Electronic spectrum, 245 nm (log  $\varepsilon$ , 4.06).

<u>3,4-Dioximino-2,2,5-trimethyl-5-phenylpyrrolidine-1-oxyl (III)</u>. To a solution of 1.55 g NH<sub>2</sub>OH·HCl in 25 ml MeOH at 0°C were added 0.74 g MeONa in 20 ml MeOH. The NaCl precipitate which formed was filtered and 1 g (II) was added. The reaction mixture was held at 20°C for 24 h, evaporated, diluted with 5 ml water, and extracted with CHCl<sub>3</sub>. The chloroform extract was dried over MgSO<sub>4</sub>. After removal of the desiccant, 3 g MnO<sub>2</sub> were added to the solution which was stirred at 20°C for 3 h. The excess oxidant was removed by filtration. The solution was evaporated and chromatographed on a column filled with silica gel (eluent was a mixture of CHCl<sub>3</sub>:MeOH, 30:1). (III) (0.5 g) and isomer (IV) (0.25 g) were separated. Found for (III): C 59.2; H 6.1; and N 15.8%.  $C_{12}H_{16}N_3O_3$ . Calculated: C 59.6; H 6.1; and

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry and N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1019-1025, May, 1989. Original article submitted February 2, 1988.



Fig. 1. Temperature dependence of  $|J_1/a|$  for two conformations of NiL<sub>2</sub> in toluene (la, b) and CHCl<sub>3</sub> (2a, b).

Fig. 2. EPR spectra of toluene glass (77 K) solutions of NiL<sub>2</sub> (1), NiL<sub>2</sub>Py (3), and the theoretically calculated spectrum (2) with:  $g_{XX} = 2.010$ ;  $g_{YY} = 2.007$ ;  $g_{ZZ} = 2.003$ ;  $A_{XX} = A_{YY} = 4.7$ ;  $A_{ZZ} = 31$ ; D = 22, J = +80,  $\Delta H = 4$  Oe;  $\alpha = \gamma = 0$ ,  $\beta = 90^{\circ}$ . Here { $\alpha, \beta, \gamma$ } are Euler angles of the main axes of the  $\hat{g}$  and  $\hat{A}$  tensors relative to the main axes of the magnetic dipole-dipole interaction.

N 16.0%. Electronic spectrum: 238 nm (log  $\varepsilon$ , 3.99). Found for (IV): C 59.3; H 6.3; and N 15.8%. Electronic spectrum: 246 nm (log  $\varepsilon$ , 4.00).

EPR spectra were recorded on PE-1306 and EPR-B radiospectrometers of the Institute of Chemical Physics, Academy of Sciences of the USSR with a thermostatted attachment and a thermostabilization accuracy of  $\pm 0.3^{\circ}$ C. The magnetic field was calibrated from spectra of Mn(II) in MgO powder. Samples for EPR experiments were prepared by a standard method, carefully removing O<sub>2</sub> and filling the ampuls with Ar. Electronic spectra were recorded on a Specord-M-40 UV-VIS spectrophotometer in a cuvette with a 1 cm path length. IR spectra were taken on a IR-71 spectrophotometer in NaCl cells.

Treatment of the experimental dependences of the |J| value on temperature and calculation of the second central moment M<sub>2</sub> in the EPR spectra (integration by the Simpson method) of complexes in frozen (77 K) solutions were obtained using a Nokia LP 4900B microprocessor pulse analyzer. Theoretical EPR spectra were calculated on a ES-1050 computer with a modernized program, the algorithm of which is described in [4]. The calculation time for one spectrum was 6-10 min.

Distances between centers of the  $\sum N-0$  groups were determined from the D value of

dipole-dipole line splitting of anisotropic EPR spectra from the formula  $r_D = 30.3(D_\perp)^{-1/3}$ [2], with  $D_\perp$  in Oe and r in Å, and from the  $M_2$  value of the second central moment of the EPR spectrum,  $r_M = 23.1 (\Delta M_2)^{-1/6}$  [2], where  $\Delta M_2 = M_2 = M_2(0)$ ,  $M_2(0)$  is the second moment of the spectrum corresponding to the monoradical in the absence of dipole-dipole interaction and r is in Å and  $\Delta M_2$  is in Oe<sup>2</sup>.

Analysis of the anisotropic EPR spectrum of HL in toluene solution at 77 K showed that the reagent is already dimerized at a concentration of  $5 \cdot 10^{-4}$  M. The mutal orientation of

N=O fragments in the dimeric molecule corresponds to an almost planar structure  $(|J| \le 15, D \ge 20$  Oe,  $r_D = 12$  Å). HL does not dimerize in ethanol up to 77 K. Dissociation  $(pK_a \ge 8)$ 



Fig. 3. Dependence of NiL<sub>2</sub> (1) and NiL<sub>2</sub>Py (2) concentration on time in the NiL<sub>2</sub>-Py-toluene system.  $C_{NiL_2}:C_{Py} = 1:100$ .

Fig. 4. Dependence of the  $|J_i/a|$  value in NiL<sub>2</sub>B on pK<sub>a</sub> of bases (B = acetone, DMSO, Py, 4-NH<sub>2</sub>Py, TEA, and Pip).

and distribution (K<sub>D</sub>  $\approx$  30) constants for HL in the CHCl<sub>3</sub>-H<sub>2</sub>O system were estimated spectro-photometrically.

NiL<sub>2</sub> were synthesized by an extraction method. The extraction conditions (Ni:HL = 1:1,  $pH_{eq} \sim 9$ , extraction time 15 min) ensured quantitative binding of the reagent by metal (extraction  $R_{Ni} > 95\%$ ). Bands at 228 (log  $\varepsilon$ , 4.2), 262 (log  $\varepsilon$ , 4.1), 315 (log  $\varepsilon$ , 3.9), 420, 450, and 560 nm were recorded in the electronic absorption spectra of the complex. Magnetic susceptibility measurements of the complex gave the value  $\mu_{eff} = 2.5$  BM, which indicates a low spin state for the central atom ( $S_{Ni} = 0$ ).

#### DISCUSSION

Exchange Interaction and Structure of NiL<sub>2</sub> in Solution. Lines corresponding to two effective conformations with slow interconversion between them are observed in the EPR spectra of NiL<sub>2</sub> both in inert aprotic and in solvating solvents over a wide temperature range (Fig. 1). The position and relative intensity of the lines for each conformation are described by one  $|J_i|$  value. The presence of two conformations is, in our opinion, related to cis and trans positions of the phenyl (Ph) group in the NiL<sub>2</sub> complex



The existence of only one conformation for the Ni complex with the symmetrical  $\alpha$ -dioxime which has a CH<sub>3</sub> instead of Ph confirms this hypothesis.

The weak temperature dependence of  $|J_i/a|$  of each NiL<sub>2</sub> conformation (Fig. 1) indicates intramolecular motion in the complex. This agrees well with the conformational mobility of the pyrrolidine ring of the ligand. This can be both twisting of the pyrrolidine ring and

vibration of the

N-0 fragments relative to each other. The effective conformational en-

thalpies calculated from the temperature dependences of  $|J_i/a|$ ,  $\Delta H_1$  and  $\Delta H_2$ , are equal to -4.3 ± 0.4 and +2.9 ± 0.9 kJ/mole in CHCL<sub>3</sub>, and -6.9 ± 2.5 and +3.7 ± 1.0 kJ/mole in toluene, respectively.

The values of  $|J_i/a|$  for the two conformations converge with decreasing temperature (Fig. 1) and are approximately equal at the freezing point of the solvent, i.e., the thermodynamically more favorable conformation of the complex is stabilized at low temperatures. The motion of the pyrrolidine ring is "frozen" at this point and the contribution of Ph to the conduction of spin density in the metal complex does not depend on its cis or trans position.



Fig. 5. Dependence of measured exchange integral value and  $a_N$  for NiL<sub>2</sub> on total solvating ability (IS\*): 1) decane; 2) heptane; 3) hexane; 4) cyclohexane; 5) di-n-butyl ether; 6) CCl<sub>4</sub>; 7) p-xylene; 8) m-xylene; 9) toluene; 10) o-xylene; 11) benzene; 12) 1,2-dichloro-ethane; 13) THF; 14) chloroform; 15) dioxane; and 16) acetone.

Analysis of the anisotropic spectrum of the toluene glass solution of  $NiL_2$  (Fig. 2) allows structural information on the thermodynamically more favorable conformation to be obtained. Theoretical calculation of the polycrystalline EPR spectra of biradicals provides

[4] a determination of the distance r between the paramagnetic groups N-O, of the mutual

orientation parameters of the fragment radical orientations (at  $r \le 13$  Å), and of the absolute value and sign of J, i.e., the structure of the biradical molecule in the glassy magnetically-dilute solution is characterized. Calculation of the theoretical EPR spectra were done with variation of all parameters of the spin-Hamiltonian which describes the intramolecular magnetic interactions. Comparison of the experimental EPR spectra of the toluene glass NiL<sub>2</sub> solution (Fig. 2) with the theoretical gave the best agreement with values of dipole interaction D = 20 Oe and J = +80 Oe. In this case, the Z axis and the  $\hat{g}$  and  $\hat{A}$ 

tensors of the N-O group are mutually parallel and perpendicular to the line joining the

centers of the radicals. The value of D found corresponds to the distance  $r_D = 11.2 \pm 0.2$  Å, which agrees well with r = 11.5 Å, calculated from x-ray data of Ni dioximates [5]. The

value r, J, and data on the mutual orientation of N-0 fragments lead to the conclusion that

the structure of the NiL<sub>2</sub> complex is planar in solution and that spin density is conducted effectively by the central diamagnetic Ni ion. The value of J in NiL<sub>2</sub> in toluene by comparison with  $(HL)_2$  is increased by >5 times.

Until now,  $\sim 20$  Ni(II) complexes with chelating spin-labeled reagents (see review [1]) have been synthesized, studied, and described in the literature. The nature of the exchange in complexes with different Ni spin states, ligand donor atoms, and structure can be compared: 1) NiO<sub>6</sub>, NiN<sub>2</sub>O<sub>4</sub>, NiN<sub>4</sub>O<sub>2</sub>, and NiN<sub>4</sub>S<sub>2</sub> have high-spin Ni(II) which leads to pairing of Ni and ligand spins or to a sharp decrease in the spin-lattice relaxation time of the spin system and an EPR spectrum is not observed, the coordination polyhedron is octahedral or pseudooctahedral; 2) NiN<sub>2</sub>O<sub>2</sub> has high-spin Ni which determines the absence of exchange between the ligand radical centers and the EPR spectrum is a triplet with |J| << a, in exact or more or less distorted tetrahedral coordination; and 3) NiN<sub>2</sub>S<sub>2</sub>, NiS<sub>4</sub> have weak exchange or its absence which are determined by the structure of reagents and extinction of J is observed in the extended organic bridge fragments, Ni is low-spin, the coordination is square planar. The  $NiL_2(NiH_4, D_4h)$  complex studied by us according to the spin state of the central atom and the structure of the coordination polyhedron should be assigned to the last group of compounds. The presence of condensed pyrrolidine and chelate rings in NiL<sub>2</sub> as well as the bond conjugations are favorable factors for existence of spin exchange between the paramagnetic centers of the ligands.

<u>EDA-Complexes.</u> Inner-sphere coordination of electron-donor compounds is usually accompanied by a change of electronic structure and geometry of the chelate. The energy of the spin exchange interaction in the biradical complex should also be changed. Data have been published on the weakening of intramolecular spin exchange in spin-labeled Cu(II)  $\beta$ -diketonates with neutral electron-donor compounds [6].

Experimental data show that interaction of NiL, with bases (B) of various nature leads to a change of the  $|J_i/a|$  value. The character of these changes depends not only on the nature of B, but also on its relative concentration and the organic solvent used. Stepwise adduct formation is observed in toluene upon reaction of NiL, with DMSO, pyridine, 4-aminopyridine, triethylamine, and piperidine. For example, a linear dependence of log CNiL, vs. time (Fig. 3) is observed with a 100-fold excess of Py relative to NiL<sub>2</sub> ( $5 \cdot 10^{-4}$  M). This corresponds to a first-order reaction and suggests the formation of the monoadduct NiL<sub>2</sub>Py which exists in solution in two conformations, similar to NiL<sub>2</sub>, with  $|J_1/a| = 2.5$  and  $|J_2/a| =$ 1.6. These values depend weakly on temperature. The biadduct NiL<sub>2</sub>Py<sub>2</sub> is formed with further increase of excess Py, for which the value is equal to zero and the EPR spectrum is a triplet. This is apparently related to the conversion of Ni into a high-spin state upon a change of the coordination polyhedron from square planar NiN, to square pyramidal  $NiN_5$  and then tetragonal bipyramidal NiN<sub>6</sub>. Displacement of the spin-labeled ligand from Ni  $\alpha$ -dioximate, which could lead to a triplet EPR spectrum, is improbable since the stability constant of  $\alpha$ -dioximates is 15-20 orders of magnitude larger than Ni pyridinates and the excess Py concentration used is relatively small.

The biadduct  $\operatorname{NiL}_2B_2$  is formed immediately upon changing toluene to  $\operatorname{CHCl}_3$  and the EPR spectrum is already a triplet with a 50-fold excess. This effect can be related to the coordination of solvent molecules by a  $\operatorname{NiL}_2$  molecule with formation of outer-sphere complexes [7]. This leads to rupture of the Ni-N bond in the equatorial plane of the coordination polyhedron and creates conditions which are favorable for adduct formation.

Formation of EDA-complexes of NiL<sub>2</sub> with imidazole (Im) in toluene gives immediately  $NiL_2Im_2$  as a result of the very low solubility of the biadduct (forms a precipitate). The composition  $NiL_2Im_2$  was confirmed by elemental analysis (Found: C 47.21; H 5.05; N 20.25; and Ni 7.55%. Calculated: C 46.60; H 5.83; N 19.42; and Ni 8.20%) and the measured value of the effective magnetic moment:  $\mu_{eff} = 3.33$  (77 K) - 3.39 (300 K) BM.  $NiL_2Im_2$  dissociates into  $NiL_2$  and Im upon dissolution in CHCl<sub>3</sub> as a result of intense competition from CHCl<sub>3</sub> for the axial coordination site.

Comparison of the anisotropic spectra of the monoadducts between themselves and with the NiL<sub>2</sub> spectra (Fig. 2) shows the monotypical spatial orientation of the fragment radicals relative to each other in these molecules. Only the |J| and D values change noticeably. These are related to the distance between unpaired electrons. The observed increase of the distances calculated from anisotropic spectra  $r_M$ , correspond to a small lengthening of the equatorial Ni-N bonds in the adducts. This can be caused by a decrease of their covalency. In turn, a decrease of the degree of covalency of the Ni-N bond upon EDA-complexation leads to a noticeable weakening of spin exchange interactions between the radical centers, which are stronger the higher the basicity of the electron-donor compounds (Fig. 4). The presence of a correlation between |J/a| and  $pK_a$  of the bases suggests a change of covalency of the planar  $\sigma$ -bonds.

<u>Solvent Effect</u>. Figure 5 shows data for  $|J_1/a|$  and  $a_N$  for NiL<sub>2</sub> in 20 different solvents. The IS\* parameter was used for solvents. This parameter characterizes the integral solvating ability [8]. The mechanism of NiL<sub>2</sub> solvation can include interaction both with the central ion and with the heteroatoms of the organic part of the molecule, including the

 $N \rightarrow 0$  groups. The dependence of the  $J_i$  value and the independence of  $a_N$  for NiL<sub>2</sub> on the nature of the solvent (Fig. 5) unambiguously attests to solvent molecule complexation not through the  $N \rightarrow 0$  group [9]. The small changes of electron conduction of the  $\sigma$ -bonds of the

bridge in the organic biradicals upon formation of biradical-solvent complexes [2] allows the dependence of  $|J_i|$  on IS\* for NiL<sub>2</sub> to be explained only due to complexation through Ni. The total interaction energy of the solvent molecules with metal complexes is rather large (25-60 kJ/mole) [7] and can lead to a change of electronic and geometric structure of the complex in solutions.

It should be noted that the nature of the change of  $|J_i/a|$  on IS\* is peculiar. The  $|J_i/a|$  value initially decreases from 2.1 (decane) to zero and then rises again to 3.8 (acetone). The shape of the EPR spectra of the biradicals in solution is determined only by the absolute value and not the sign of J [2]. Therefore, the dependence observed in Fig. 5 is most likely explained by a change in the sign of J (for example, see [10]) which can be related to a change of symmetry of the NiL<sub>2</sub> complex upon its solvation.

The authors thank A. A. Shubin for supplying the programs for calculation of theoretical EPR spectra and V. N. Ikorskii for measurement of magnetic susceptibilities.

## CONCLUSIONS

1. The low-spin Ni(II) ion in the square planar spin-labeled  $\alpha$ -dioximate NiL<sub>2</sub> effect-

ively exchanges spin density between the N-0 groups of the ligands.

2. Stepwise adduct formation  $NiL_2 \rightarrow NiL_2B \rightarrow NiL_2B_2$  in the Ni-HL-toluene-neutral electron-donor compound system is observed and studied. Adduct formation is found to lead to a decrease of the value of the spin exchange integral |J| as a result of a decrease of the degree of covalency of the Ni bond with the ligand donor atoms in the equatorial plane.

### LITERATURE CITED

- 1. S. V. Larionov, Zh. Strukt. Khim., 23, 125 (1982).
- 2. V. N. Parmon, A. I. Kokorin, and G. M. Zhidomirov, Stable Biradicals [in Russian], Nauka, Moscow (1980).
- 3. V. A. Reznikov and L. B. Volodarskii, Inventor's Certificate No. 1,244,145 (USSR), Byull. Izobret., No. 26 (1986).
- 4. V. N. Parmon, A. I. Kokorin, and G. M. Zhidomirov, J. Magn. Reson., 28, 339 (1977).
- 5. É. A. Gilinskaya and M. A. Porai-Koshits, Foundations of Science. Ser. Chemistry.
- Crystal Chemistry [in Russian], Izd. VINITI, Moscow (1970), No. 5, p. 152.
- 6. O. M. Petrukhin and V. Yu. Nad', Koord. Khim., <u>9</u>, 298 (1983).
- 7. V. M. Nekipelov and K. I. Zamaraev, Zh. Strukt. Khim., 24, 133 (1983).
- 8. V. S. Shmidt, É. A. Mezhov, and S. S. Novikova, Radiokhimiya, 9, 700 (1967).
- 9. A. L. Buchachenko and A. M. Vasserman, Stable Radicals [in Russian], Khimiya, Moscow (1973).
- 10. A. I. Kokorin, A. A. Shubin, and V. N. Parmon, Izv. Akad. Nauk SSSR, Ser. Khim., 2023 (1981).