# Effect of a metal ion on intramolecular spin exchange in spin-labeled complexes

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The characteristic features of intramolecular spin exchange in 14 complexes of $Ag^I$, $Hg^{II}$, $Ni^{II}$, $Pd^{II}$, $Pt^{II}$, $Au^{III}$, and $Pt^{IV}$ with spin-labeled ligands were studied by ESR spectroscopy. The measured values of the exchange integral $|J|$ and the differences between the enthalpies of the efficient conformations ($\Delta H$) were compared with the electronic polarization (refraction) $R_r$ of the $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ ions and Klopman's rigidity parameters $\sigma_K$, which characterize the total polarazibility of the ions and the degree of covalence of the bond between the metal atom and the donor atom of the ligand, respectively. Delocalization of the electron spin density and the efficiency of spin exchange are determined by the relative contributions of the s, p, and d orbitals, which produce the overlap integral of wave functions, $|J|$, and by the geometric features of the coordination polyhedron, which affect the mutual orientation of the N—O fragments.

**Key words:** noble metals, nitroxyl radicals metal complexes, structure, spin exchange ESR spectra.

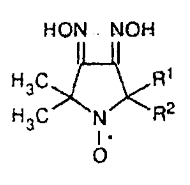
A great number of works were devoted to studies of metal complexes with spin-labeled ligands, *viz.*, with stable nitroxide radicals (see, for example, Refs. 1—4 and references therein). These compounds are of great interest in analytical chemistry[5] as well as in the chemistry of antitumor drugs.[6] Investigations of these compounds provide unique information on the structures, physicochemical properties, and characteristic features of delocalization of the electron spin density over the atoms and bonds in the polyhedron, which is essential to understanding the mechanisms of homogeneous catalysis. By analogy with organic biradicals,[7] it is believed that intramolecular spin exchange in metal complexes with two molecules of a spin-labeled reagent depends primarily on the electronic and spin states of the central atom, the degree of covalence of the donor atom—metal bond, and the spatial structure of the metal complex.[7,8]

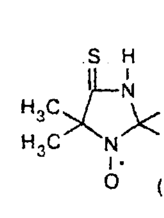
Analysis of the published data demonstrated that the effects of the radical structure, the presence of acceptor substituents in the nitroxyl ring and in the organic bridge, adduct formation, and solvation on the efficiency of spin exchange coupling in doubly spin-labeled metal complexes have been adequately revealed, while the role of the nature of the coordinating metal ion is still not clearly understood. Abundant experimental data on complexes with paramagnetic ions, *viz.*, with $Cu^{II}$, $Fe^{III}$, $Co^{II}$, $Cr^{III}$, $VO^{II}$, $Ni^{II}$, *etc.*,[2,4,8] were accumulated in connection with attempts to design new organic ferromagnets and high-temperature superconductors based on these multispin compounds.

The main aim of the present work is to elucidate the effect of the nature of the diamagnetic coordinating ion on intramolecular spin exchange in doubly spin-labeled metal complexes. The formalism, which was developed for stable organic biradicals,[7] can be extended to the compounds under consideration.

## Experimental

Stable nitroxyl radicals $HL^1$ — $HL^4$ used in this work were synthesized according to known procedures.[5,9]





($HL^4$)

$R^1 = R^2 = Me$ ($HL^1$)
$R^1 = Me$, $R^2 = Ph$ ($HL^2$)
$R^1 = R^2 = Ph$ ($HL^3$)

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The spin-labeled nickel(II), palladium(II), and platinum(II) α-dioximates were synthesized starting from the salts $Ni(NO_3)_2 \cdot 6H_2O$ of analytical grade, $K_2PdCl_4$, $K_2PtCl_4$, and $Pd(MeCOO)_2$ of chemically pure grade, and $H_2PtCl_6 \cdot 6H_2O$, $HAuCl_4 \cdot 3H_2O$, and $AgNO_3$ (Aldrich) of analytical grade. Chloroform was purified by washing six times with an equal volume of distilled water, dried with anhydrous $CaSO_4$, and distilled. Chemically pure toluene was used in spectroscopic studies without additional purification.

All $ML_2{}^1$, $ML_2{}^2$, and $ML_2{}^3$ compounds ($M = Ni^{II}$, $Pd^{II}$, or $Pt^{II}$) were prepared by extraction using reagents taken in an [M] : [L] ratio of 1 : 1, which enabled quantitative binding of the reagent with metal. The $NiL_2$ complexes were synthesized at pH ~ 9; the time of extraction was 15 min. To prepare $PdL_2$ from $Pd(MeCOO)_2$, a solution of the reagent (0.01 mmol) in $CHCl_3$ (4 mL) was added to a solution of the salt (0.01 mmol) in $CHCl_3$ (1 mL) and the reaction mixture was refluxed at 95 °C on a water bath for 30 min. After cooling and centrifugation, the organic phase was separated. The $PtL_2$ and $PdL_2$ complexes were synthesized from $K_2PtCl_4$ and $K_2PdCl_4$, respectively, by adding a solution of the reagent (0.02 mmol) in $CHCl_3$ to the salt (0.01 mmol) in an aqueous solution of $Na_2B_4O_7$ (5 mL, 0.2 mol). The reaction mixture was refluxed at 95 °C on a water bath for 5 h. After cooling and centrifugation, the organic phase was separated and shaken 3—5 times with an equal volume of 0.01 *M* NaOH solution to remove the unconsumed reagent (the complete removal of the reagent was monitored by ESR spectroscopy).

The $Ag^I$, $Au^{III}$, $Hg^{II}$, $Pd^{II}$, and $Pt^{IV}$ complexes with $HL^4$ were prepared by extraction from acidic (0.3 mol $L^{-1}$ HCl) and alkaline (0.05 mol $L^{-1}$ $Na_2B_4O_7$) solutions. To exclude the contribution of noncoordinated $HL^4$ molecules to the ESR spectrum, the amounts of $HL^4$ used in the extraction from acidic solutions were smaller than those which were necessary as regards the stoichiometry. In the case of extraction from alkaline solutions, an excess of the reagent was removed by washing the extract with a NaOH solution (0.01 mol $L^{-1}$). This procedure made it possible to prevent the effect of hydrolysis at high concentrations of metal ions. All the above-mentioned complexes were studied immediately after preparation without isolation in the solid state. The duration of extraction ensured quantitative binding of the reagent with metal. In the cases of $Ni^{II}$, $Hg^{II}$, $Pd^{II}$, and $Pt^{IV}$, the degree of extraction $R_M > 95\%$. In the cases of $Ag^I$ and $Au^{III}$, the degree of extraction $R_M > 75\%$.[5]

For the mercury compound, the $HgL_2{}^4$ composition was confirmed by the data of elemental analysis (found (%): C, 31.05; H, 4.15; S, 11.75; calculated (%): C, 30.88; H, 4.78; S, 11.76) and by the average molecular weight of 546 (the calculated value is 544). In addition, the binuclear $Pd_2L_4{}^4$ complex was isolated from the alkaline solution (found (%): C, 37.59; H, 5.28; N, 12.30; S, 14.74; Pd, 23.10; for $(C_{14}H_{24}N_4S_2PdO_2)_n$ calculated (%): C, 37.29; H, 5.37; N, 12.42; S, 14.22; Pd, 23.60; the average molecular weight was 900; the calculated value is 902).[10]

The ESR spectra were recorded on an X-band Varian E-4 radiospectrometer equipped with a temperature-controlled attachment in thin-walled quartz tubes (the temperature was maintained within ±0.5°). The magnetic field was calibrated using $Mn^{2+}$ ions in the MgO matrix as the standard. The ESR spectra were recorded using samples which were thoroughly purified from oxygen, and tubes were filled with argon. The measurements of the constants of hyperfine interactions between the unpaired electron and the $^{14}N$ nucleus ($a^N$) and the calculations of the exchange integrals $|J/a|$, the differences between the enthalpies of the efficient conformations $\Delta H$, and the distances $r$ between the unpaired electrons of the N—O groups were carried out according to known procedures.[7]

## Results and Discussion

The metal complexes extracted with spin-labeled reagents are generally coordination compounds in which the central metal ion and the nearest coordination sphere can be distinguished. The nature of the metal atom and the type of the donor atom—metal bond in spin-labeled biradical complexes $ML_2$ are of decisive importance in the realization of intramolecular indirect spin exchange.

To obtain an adequate relationship between the efficiency of spin exchange coupling and the properties of the central atom, it is necessary to vary metal ions with retention of the coordination polyhedron and the spatial structure of the complex as a whole. In this case, one can solve a complicated problem associated with the separation of the electronic and geometric (orientational) contributions to the spin conductivity of the bridging atoms. The nickel(II), palladium(II), and platinum(II) complexes with spin-labeled α-dioximes $HL^1$, $HL^2$, and $HL^3$ were synthesized and studied as the first model systems. The complexes chosen allow one to consider the effect of the electronic structure of the central atom on the spin conductivity, with the geometry being the same. X-ray diffraction analysis of a series of α-dioxime complexes with different structures[11—13] demonstrated that $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ α-dioximates are isostructural.

Typical isotropic ESR spectra of dilute solutions of the $NiL_2{}^1$, $PdL_2{}^1$, and $PtL_2{}^1$ complexes in chloroform at 293 K are shown in Fig. 1. The positions and the

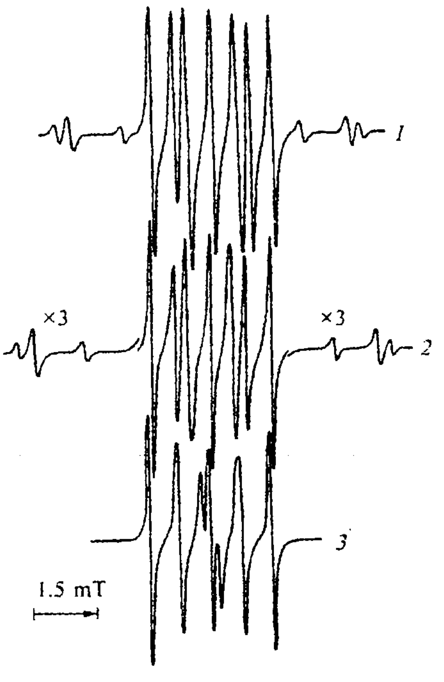


**Fig. 1.** ESR spectra of solutions of the complexes $NiL_2{}^1$ (*1*), $PdL_2{}^1$ (*2*), and $PtL_2{}^1$ (*3*) in chloroform at 293 K. $[ML_2{}^1] = 5 \cdot 10^{-4}$ mol $L^{-1}$.

**Table 1.** Exchange integrals $|J/a|$ and the hyperfine interaction constants $a^N$ for the $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ complexes in chloroform at 293 K

| Metal | Ionic radius/Å[a] | $R_f$[b]/cm$^3$ | $\sigma_K$[c] | $\|J/a\|\pm0.1$ $[a^N\pm0.1/G]$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $ML_2^1$ | $ML_2^2$ (*A*) | $ML_2^2$ (*B*) | $ML_2^3$ (*A*) | $ML_2^3$ (*B*) |
| Ni | 0.74 | 1.9 | −0.70 | 1.8 | 8.1 | 2.2 | 10.4 | 3.7 |
| Pd | 0.83 | 3.3 | −3.05 | 2.5 | 9.5 | 5.1 | 11.4 | >13.0 |
| Pt | 0.85 | 3.8 | −3.25 | 7.4 | >13.5 | >13.5 | >14.0 | >14.0 |
| | | | | [14.7] | [14.6] | [14.6] | [14.5] | [14.5] |

[a] For a coordination number of 4.[14]

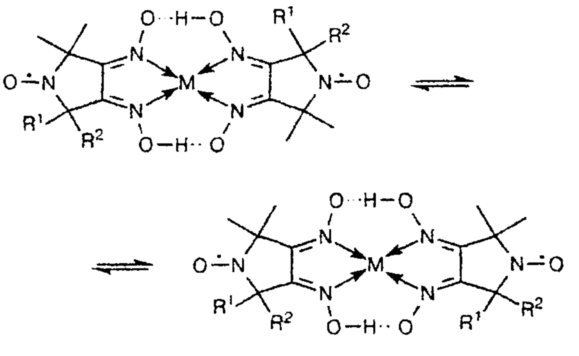
[b] The electronic polarization (refraction).[14]

[c] Klopman's rigidity parameter.[15]

intensity ratios of the lines in the spectra and the absence of a temperature dependence of the exchange integral $|J|$ allow the conclusion that the $ML_2^1$ complexes exist in solutions as only one conformer. The $|J|$ values (for convenience of comparison, these values are generally expressed in terms of the hyperfine interaction constant $a^N$, *i.e.*, as $|J/a|$) are given in Table 1.

The $ML_2^2$ and $ML_2^3$ compounds exist in solutions as two conformers[7] that differ in the value of $|J|$ (see Table 1), the slow interconversion of these conformers being observed. The presence of two conformations is attributable to the *cis* and *trans* arrangement of the phenyl substituents in the complexes (Scheme 1).

**Scheme 1**



From Table 1 it follows that the exchange integral $|J/a|$ increases in the series $Ni^{II} < Pd^{II} < Pt^{II}$ for all the spin-labeled α-dioximates under study. Taking into account the fact that the complexes are isostructural, the observed increase in the $|J|$ value may be associated only with the differences in the electronic structure of the metal ion and in the type of the M—N bond. The electronic polarizations (refractions) $R_f$ of the $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ ions and Klopman's rigidity parameters $\sigma_K$ are given in Table 1. These parameters, which characterize the total polarizability of the ions and the degree of covalence of the bond between the metal atom and the donor atom of the ligand, respectively, correlate well with each other and qualitatively correlate with the $|J/a|$ values. The results obtained allow the conclusion that the spin exchange coupling increases as the polarizability of the central atom and the degree of covalence α of the M—N bond increase in the $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ series. This sharp enhancement of exchange is qualitatively consistent with the ratio $|J| \sim \alpha^4$ obtained according to Anderson's theory.[16]

The introduction of acceptor substituents into the pyrrolidine ring leads to redistribution of the electron and spin density in the ring. Thus for conformations *A* of the $HL^2$ and $HL^3$ ligands (see Table 1), as in the case of $HL^1$, the $|J/a|$ value moderately increases in going from $Ni^{II}$ to $Pd^{II}$ and sharply increases in going from $Pd^{II}$ to $Pt^{II}$. For conformations *B* (see Table 1), the inverse dependence is observed.

The subsequent extraction syntheses of the complexes with the use of the $HL^4$ radical reagent were performed both in acidic and alkaline media. The choice of this ligand was determined by the fact that the sizes of the resulting metal complexes are close to those of the complexes with α-dioximes. For example, for the complexes extracted from acidic media, the distances *r* between the midpoints of the N—O groups are 11.1±0.2, 11.2±0.2, and 10.9±0.3 Å in $NiL_2^1$,[17] $NiL_2^2$,[9] and $PdL_2^4$,[10] respectively. Unlike the known analytical reagent 2-mercaptobenzothiazole,[18] the $HL^4$ radical does not extract $Ni^{II}$ ions from aqueous solutions. The concentrations of the $Pt^{IV}$ complexes extracted from acidic media were so low that we failed to record the ESR spectrum.

It can be seen from Fig. 2 that the character of the ESR spectra of the complexes (except for those of the $Pd^{II}$ ion in an alkaline medium) is characteristically biradical, which indicates that the coordination polyhedra of the compounds extracted contain two ligand molecules. From the temperature dependences of the $|J/a|$ values (Fig. 3) it follows[7] that all the complexes under study exist in solutions as at least two conformers, which are rapidly interconverted, and the measured

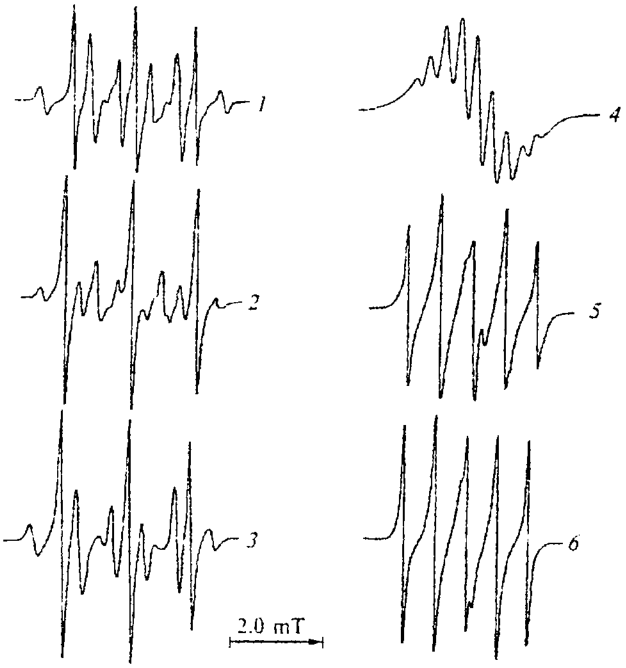


**Fig. 2.** ESR spectra of solutions of the $ML_2^4$ complexes after extraction from acidic media (*1—3*) with a chloroform solution of $HL^4$ and after washing with a NaOH solution (0.01 mol $L^{-1}$) (*4—6*) at 298 K. *1* and *4*, $Pd^{II}$; *2* and *5*, $Au^{III}$; *3* and *6*, $Hg^{II}$. $[ML_2^4] < 5 \cdot 10^{-4}$ mol $L^{-1}$.

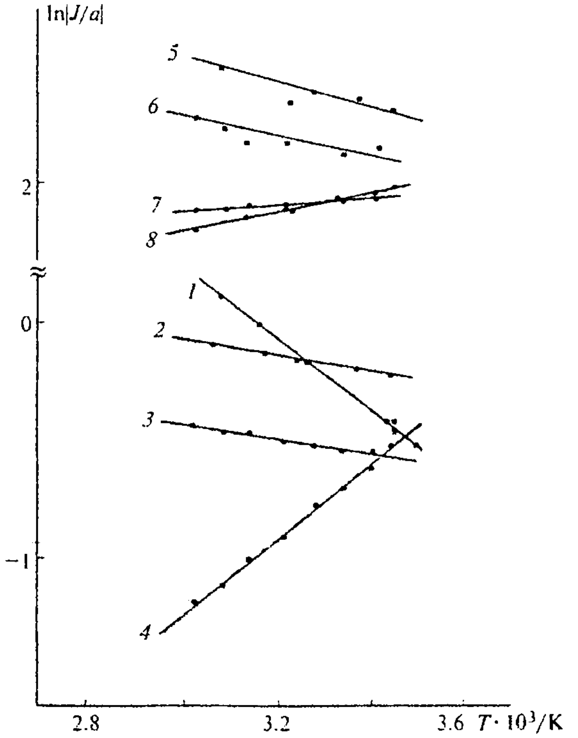
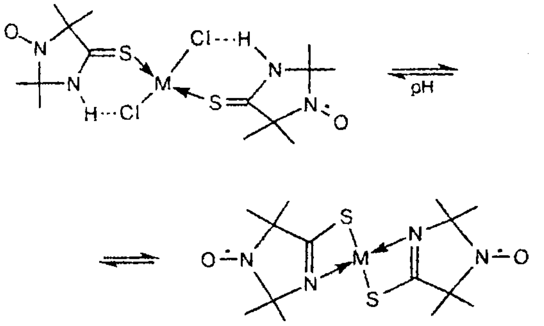


**Fig. 3.** Temperature dependence of $|J/a|$ for the $ML_2^4$ complexes extracted with chloroform from acidic (*1—4*) and alkaline (*5—8*) media: *1* and *5*, $Hg^{II}$; *2*, $Pd^{II}$; *3* and *6*, $Ag^{I}$; *4* and *7*, $Au^{III}$; *8*, $Pt^{IV}$.

value of $|J|$ is averaged. The difference between the enthalpies of the conformations $\Delta H$ (Table 2) corresponds to the energy of vibration or hindered rotation of the radical fragments with respect to the central ion.

Analysis of the ESR spectra demonstrated that the $|J/a|$ values substantially increase (by a factor of 14.2±0.6 for $Ag^{I}$, $Hg^{II}$, and $Au^{III}$; see Table 2) in going from acidic to alkaline media. In this case, the intramolecular rigidity of the polyhedron also increases, as follows from Fig. 3 and from the change in the parameter $\Delta H$ (see Table 2). The spin exchange coupling is enhanced, due, apparently, to an increase in the degree of covalence of the bond between the metal atom and the donor atom of the ligand. The data in Table 2 suggest that the mode of coordination of the ligands in the complexes changes from monodentate through the S atom to bidentate through the S and N atoms as the pH of the extraction process increases (Scheme 2).

**Scheme 2**



It was demonstrated that the $Pd^{II}$ compounds, unlike compounds with the other ions under study, form the binuclear $Pd_2L_4^4$ complexes rather than the $PdL_2^4$ complexes. The composition and the structure of the $Pd^{II}$ compound were confirmed by X-ray diffraction analysis and ESR spectroscopy.[10]

**Table 2.** Exchange integrals $|J/a|$ at 298 K and the differences between the enthalpies ($\Delta H$) of the efficient exchange conformations of the metal complexes $ML_2^4$ with the $HL^4$ radical extracted from acidic and alkaline media

| Metal | Acidic medium | | Alkaline medium | |
|---|---|---|---|---|
| | $\Delta H$ /kJ $mol^{-1}$ | $\|J/a\|$ | $\Delta H$ /kJ $mol^{-1}$ | $\|J/a\|$ |
| $Pd^{II}$ | 3.0±0.5 | 0.84±0.05 | — | >>1.0 |
| $Hg^{II}$ | 12.0±1.2 | 0.73±0.05 | 2.7±3.0 | 10.5±0.1 |
| $Ag^{I}$ | 2.5±0.4 | 0.57±0.05 | 2.6±0.6 | 8.6±0.1 |
| $Au^{III}$ | −13.0±0.5 | 0.52±0.05 | −1.3±0.5 | 7.0±0.1 |
| $Pt^{IV}$ | — | — | −3.3±0.6 | 7.0±0.1 |

*Note.* Acidic medium, 0.3 *M* HCl; alkaline medium, 0.01 *M* NaOH.

Noteworthy is the difference in the character of the changes of $|J/a|$ in the series of compounds with $HL^{1-3}$ and $HL^4$ (see Tables 1 and 2). In the first case, the $|J|$ value increases as the number of the row to which the complex-forming metal belongs increases. In the second case, the inverse dependence is observed (see the $Pd^{II}$—$Pt^{IV}$ and $Ag^{I}$—$Au^{III}$ pairs). In this case, the electronic state of the ion and fine geometric features of the polyhedra play, apparently, a decisive role. The particular contributions of the s, p, and d orbitals, which form the overlap integral and thereby determine the $|J|$ value, depend on the above-mentioned factors.

This explanation is in agrrement with the published data[19] on intramolecular spin exchange in isostructural binuclear $Pd^{II}$ complexes with spin-labeled chelate reagents L of composition $[PdLX]_2$, in which the Pd atoms are linked through bridges formed by two X atoms ($Cl^-$, $Br^-$, or $I^-$). The observed increase in the $|J/a|$ value in the series $Cl^- < Br^- < I^-$ correlates well with the data on the efficiency of electron transfer through analogous bridges in reduction reactions of the complexes.[20] We believe that the reason is that in this case, like in $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ α-dioximates, the extent to which the d orbitals are involved in the transfer of the spin density increases as the polarizabilities of the bridging atoms increase ($R_f = 8.3 < 11.5 < 17.5$ cm$^3$ in the series $Cl^-$—$Br^-$—$I^-$, respectively[14]).

The results obtained demonstrate that delocalization of the electron spin density and the efficiency of spin exchange coupling in metal complexes with spin-labeled ligands are determined by two major factors associated with the nature of the central metal atom, *viz.*, by the relative contributions of the s, p, and d orbitals, which produce the overlap integral of wave functions, *i.e.*, the $|J|$ value, and by the geometric features of the coordination polyhedron, which affect the mutual orientation of the paramagnetic nitroxyl fragments.

Actually, the $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ α-dioximates under study belong (as regards the structure of the coordination polyhedron) to the symmetry group $D_{4h}$ (a planar square), $Ni^{II}$ existing in the low-spin state.[8,9] The presence of the fused chelate and pyrrolidine rings in $ML_2^{1-3}$ as well as the conjugation of the bonds are favorable for the occurrence of spin exchange interactions between the $N-\dot{O}$ groups of the ligands. In the case of the $ML_2^4$ complexes, the situation is substantially more complicated. It is known[3,4,11,12] that $Ni^{II}$, $Pd^{II}$, $Pt^{II}$, and $Au^{III}$ compounds have the $d^8$ configuration with the planar-square structure, $Ag^I$ and $Hg^{II}$ complexes are generally linear or planar and have the $4d^{10}$ and $5d^{10}$ configurations, respectively, and $Pt^{IV}$ complexes adopt the $5d^6$ configuration and are characterized by distorted octahedral structures.

## References

1. S. S. Eaton and G. R. Eaton, in *Spin Labeling III*, Ed. L. J. Berliner, Plenum, New York, 1989.
2. K. M. More, G. R. Eaton, S. S. Eaton, O. H. Hankovszky, and K. Hideg, *Inorg. Chem.*, 1989, **28**, 1734.
3. *Imidazoline Nitroxides. Synthesis, Properties, Applications*, Ed. L. B. Volodarsky, CRC Press, Boca Raton, Florida, 1988, V. 2.
4. G. V. Romanenko, N. V. Podberezskaya, and N. V. Pervukhina, *Zh. Strukt. Khim.*, 1988, **34**, No. 3, 119 [*J. Struct. Chem.*, 1988, **34** (Engl. Transl.)].
5. N. G. Vanifatova, M. V. Evstiferov, and V. V. Martin, *Zh. Anal. Khim.*, 1988, **43**, 435 [*Sov. J. Anal. Chem.*, 1988, **43** (Engl. Transl.)].
6. V. D. Sen', A. V. Kulikov, A. V. Shugalii, and N. P. Konovalova, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1640 [*Russ. Chem. Bull.*, 1998, **47**, 1598 (Engl. Transl.)].
7. V. N. Parmon, A. I. Kokorin, and G. M. Zhidomirov, *Stabil'nye biradikaly* [*Stable Biradicals*], Nauka, Moscow, 1980 (in Russian).
8. S. V. Larionov, *Zh. Strukt. Khim.*, 1982, **23**, No. 4, 125 [*J. Struct. Chem.*, 1982, **23** (Engl. Transl.)].
9. M. V. Evstiferov, N. G. Vanifatova, and O. M. Petrukhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1019 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 921 (Engl. Transl.)].
10. M. V. Evstiferov, N. G. Vanifatova, O. M. Petrukhin, A. I. Kokorin, and L. B. Volodarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2489 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2241 (Engl. Transl.)].
11. E. A. Gilinskaya and M. A. Porai-Koshits, *Itogi nauki i tekhniki. Kristallokhimiya* [*Results of Science and Engineering. Crystal Chemistry*], VINITI, Moscow, 1970, **5**, 152 (in Russain).
12. *Kristallicheskie struktury neorganicheskikh soedinenii* [*Crystal Structures of Inorganic Compounds*], Ed. T. I. Malinovskii, Shtiintsa, Kishinev, 1974 (in Russian).
13. L. F. Lindoy, S. E. Livingstone, and N. C. Stephenson, *Inorg. Chim. Acta*, 1967, 161.
14. S. S. Batsanov, *Eksperimental'nye osnovy strukturnoi khimii. Spravochnoe posobie* [*Experimental Fundamentals of Structural Chemistry. Handbook*], Izd-vo Standartov, Moscow, 1986 (in Russian).
15. O. M. Petrukhin, in *Khimiya ekstraktsii* [*Chemistry of Extraction*], Nauka, Novosibirsk, 1984, 112 (in Russian).
16. P. W. Anderson, *Phys. Rev.*, 1959, **115**, 2.
17. M. V. Evstiferov, N. G. Vanifatova, O. M. Petrukhin, A. I. Kokorin, V. A. Reznikov, and L. B. Volodarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1152 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1047 (Engl. Transl.)].
18. E. S. Raper, *Coord. Chem. Rev.*, 1985, **65**, 115.
19. A. I. Kokorin, V. N. Parmon, V. I. Ovcharenko, S. V. Larionov, and L. B. Volodarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1763 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **37** (Engl. Transl.)].
20. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solutions*, 2nd Ed., J. Wiley, New York—London—Sydney, 1967.

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