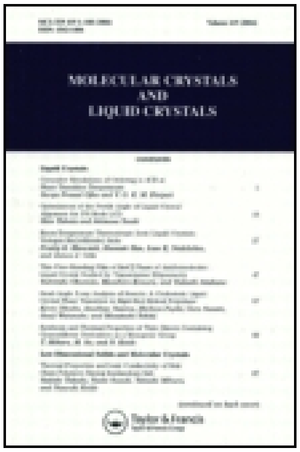

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Complexes with Nitr' oxides Containing Different Substituents in the α-Position to N··O Group Competition of Basicity and Sterical Availability of the Donor Functions of Nitroxides in Metal Complexes with Sterically Hindered Imidazolines

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COMPLEXES WITH NITROXIDES CONTAINING DIFFERENT SUBSTITUENTS IN THE α-POSITION TO N•-O GROUP. COMPETITION OF BASICITY AND STERICAL AVAILABILITY OF THE DONOR FUNCTIONS OF NITROXIDES IN METAL COMPLEXES WITH STERICALLY HINDERED IMIDAZOLINES

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Abstract In the nitroxide molecule, change of the substituent in the α-position to the N•-O group affects both the donor properties of this group and its steric availability. Metal complexes with three nitroxide pairs are used to show that the above change of the α-substituent in the nitroxide molecule can induce structural transformation of the molecular complex itself (and, as a consequence, change its magnetic properties), change the magnetic properties of the solid complex, or change the chemical behavior of the nitroxide.

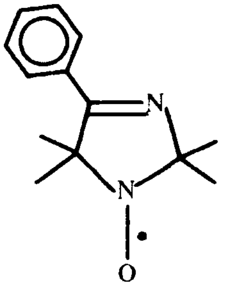
INTRODUCTION

Complexation of paramagnetic ions of transition metals with stable nitroxides is a convenient method of the synthesis of heterospin molecules.[1-4] For the transition from these molecules to chain, layered, and frame structures capable of magnetic ordering at temperatures higher than 4.2 K, the N•-O groups should be coordinated by the paramagnetic metal ions, which provides an effective exchange channel. In the absence of this coordination in polymeric heterospin systems, magnetic ordering is possible only at very low temperatures (below the liquid helium temperature).[1,4] However, almost all currently known stable nitroxides have sterically hindered donor N•-O group. Therefore, both the donor properties of the N•-O group and its steric availability should be considered. This problem has not been studied systematically, although such investigations would be very important for the design of heterospin systems with 2-D and 3-D structures in solid. As a rule, the syntheses of metal complexes with nitroxides are carried out with unchanged environments of N•-O groups. Thus, the steric factor is not considered. Changing the substituent in the α-position to the N•-O group affects both its donating ability and steric availability. This can change either the manner of coordination of the paramagnetic ligand, i.e., the structure and magnetic properties of the molecular complex, or the structure and magnetic properties of the complex in solid. Changing the substituent in α-position to N•-O group can also significantly affect the chemical behavior of the nitroxide. In this work, these effects are considered in metal complexes with three different nitroxide pairs.

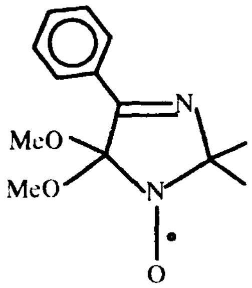
FIRST PAIR

A Change in the donor properties of a nitroxide causes a change in the molecular structure of the metal complex with the nitroxide

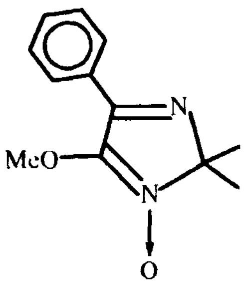
The nitroxides L^1 and L^2 included in the first pair are very similar. The structural difference is in the 5-substituents in 3-imidazoline heterocycle, methyl and methoxy groups in L^1 and L^2, respectively. The methoxy groups possess the property of strong electron density withdrawing. Therefore, the donating ability of the >N-•O group oxygen and imine nitrogen of L^2 is essentially lower than that of L^1. This leads to different products and different molecular structures of the complexes resulting from the reactions of L^1 and L^2 with Co(II) or Ni(II) hexafluoroacetylacetonate.[5]



L^1



L^2



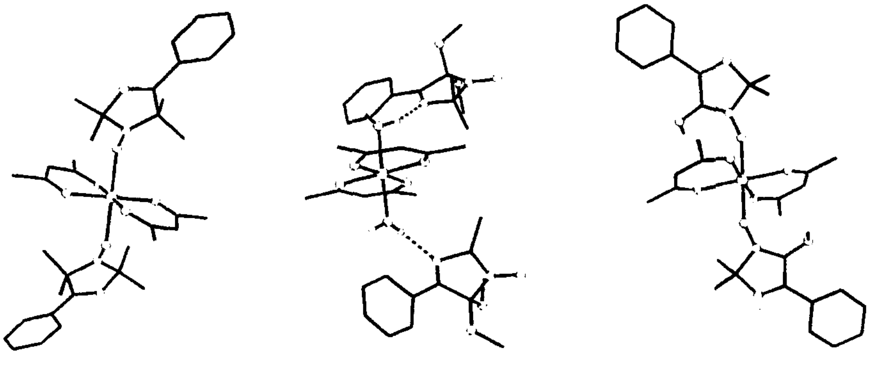
L^3

Heating Co(II) or Ni(II) hexafluoroacetylacetonate with nitroxide L^1 in hexane or heptane shifts equilibrium (1) to the right, with water removed from the reaction mixture. With water present in the mixture, equilibrium (1) is shifted to the left, since the donating ability of water molecules is higher than that of L^1. Due to steric hindrances in $M(hfac)_2(L^1)_2$, where M = Co and Ni, the nitroxides are bound to metal ions through the less basic nitroxyl oxygens, while the more basic imine nitrogens do not participate in the coordination (Fig. 1).

$$\begin{array}{lll} M(hfac)_2\,nH_2O_{(solv)} + 2L^1_{(solv)} \rightleftarrows & M(hfac)_2(L^1)_{2(solv)} + nH_2O_{(gas)} & \\ \downarrow\uparrow & \downarrow\uparrow & (1) \\ M(hfac)_2\,nH_2O_{(solid)} & M(hfac)_2(L^1)_{2(solid)} & \end{array}$$

An attempt to synthesize water-free complexes with L^2 in a similar manner was unsuccessful. $Ni(hfac)_2(H_2O)_2(L^2)_2$ was the only product, and the reaction of $Co(hfac)_2{\cdot}nH_2O$ with L^2, after removing water, yielded a complex with the corresponding nitrone $Co(hfac)_2(L^3)_2$. The complex $Co(hfac)_2(H_2O)_2(L^2)_2$ was synthesized by gradual evaporation of ether from a heptane-ether mixture of the reagents. In $M(hfac)_2(H_2O)_2(L^2)_2$, the coordinated water molecules act as spacers and the steric hindrances in the ligands determine the H-bonding between the coordinated water molecules and the imine nitrogens of L^2 (Fig.1). It is noteworthy that the methoxy oxygen atoms also participate in the H-bonding with neighbouring molecules. L^2, which is less basic than L^1, is incapable of replacing water in the coordination sphere of $M(hfac)_2(H_2O)_2(L^2)_2$.

$M(hfac)_2(L^1)_2$ demonstrate the strong antiferromagnetic coupling between the metal ion and nitroxides ($J \approx -350$ cm^{-1} for M=Ni), whereas $M(hfac)_2(H_2O)_2(L^2)_2$ have no exchange clusters with exchange interaction energies higher than $|5|$ cm^{-1}. A comparison between the magnetic properties of $Ni(hfac)_2(L^2)_2$ and $Ni(hfac)_2(H_2O)_2(L^2)_2$ provides one more evidence for a strong decrease in the exchange interaction energy in the presence of bridging water molecules between paramagnetic centres.[6]



$M(hfac)_2(L^1)_2$ $M(hfac)_2(H_2O)_2(L^2)_2$ $Co(hfac)_2(L^3)_2$

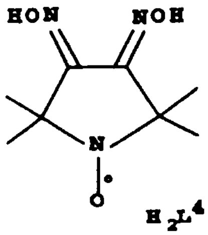
FIGURE 1 Structures of the molecules.

Thus, the substitution of methyl groups in the α-position to nitroxyl by electron-density-withdrawing methoxy groups decreases the donating ability of the >N-•O group. This is the reason why L^2, being less basic than L^1, is incapable of replacing water in the coordination sphere of $M(hfac)_2(H_2O)_2(L^2)_2$. This phenomenon is unfavorable in designing molecular magnets based on transition metal complexes with nitroxides. On the other hand, steric hindrances caused by bulky substituents around the imine nitrogen can result in the coordination of the nitroxyl oxygen by the metal ion like in $M(hfac)_2(L^1)_2$. This is favourable for the formation of the M-O•-N< bonds and, as a consequence, for the design of molecular magnets.

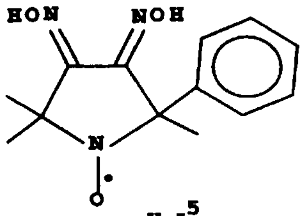
SECOND PAIR

A change in the steric availability of the nitroxyl group causes a change in the magnetic properties of the solid complex

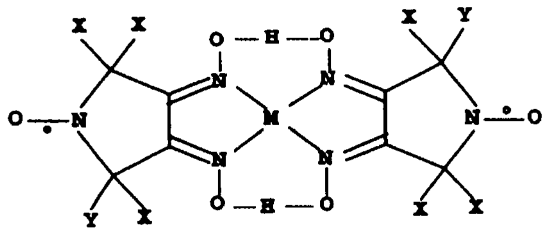
The second pair of nitroxides under investigation consists of the dioximes H_2L^4 and H_2L^5. They are also very similar paramagnetic ligands. The only structural difference is in the substituent Y in the 2-position of pyrrolidine heterocycle.



H_2L^4



H_2L^5



$X,Y = CH_3$ $M(HL^4)_2$

$X = CH_3, Y = C_6H_5$ $M(HL^5)_2$

$M = Ni, Pd$

The $M(HL^4)_2$ and $M(HL^5)_2$ complexes, where M = Ni, Pd, were synthesized in methanol or water-methanol solutions by the following reactions:

$$Ni(CH_3COO)_2 + 2H_2L^{4,5} + 2(C_2H_5)_3N \longrightarrow Ni(HL^{4,5})_2 + 2(C_2H_5)_3NHOOCCH_3$$

$$K_2PdCl_4 + 2H_2L^{4,5} + 2KOH \longrightarrow Pd(HL^{4,5})_2 + 4KCl + 2H_2O$$

The Ni(II) and Pd(II) dioximes are very good model molecules because of the same square-planar coordination of the central atoms. Both metals are diamagnetic. Thus, in fact, the $M(HL^4)_2$ and $M(HL^5)_2$ molecules are biradicals. In such systems, exchange interactions are caused by interactions only between unpaired electrons of N•-O centers. In $M(HL^4)_2$ and $M(HL^5)_2$ in solutions, the exchange interactions were investigated by the ESR method in the study of the solution extraction of metal ions with spin-labelled dioximes.[7,8] It has been established that the magnetic properties of $M(HL^4)_2$ and $M(HL^5)_2$ are very similar and in the bischelate molecules the intramolecular exchange energies are very low (below 26.5-139 G).

We prepared $M(HL^4)_2$ and $M(HL^5)_2$ as individual solids and investigated their magnetic behavior. It has been determined that in solid $M(HL^4)_2$ the intermolecular exchange is significantly higher than that in solid $M(HL^5)_2$ (in the frozen solutions of the complexes, no intermolecular exchange interactions were detected). For instance, $J = -22.3$ cm^{-1} for $Ni(HL^4)_2$ and $J = -6.5$ cm^{-1}for $Pd(HL^4)_2$. For $Ni(HL^5)_2$ and $Pd(HL^5)_2$, the values of J are less than 1 cm^{-1} (Fig. 2).

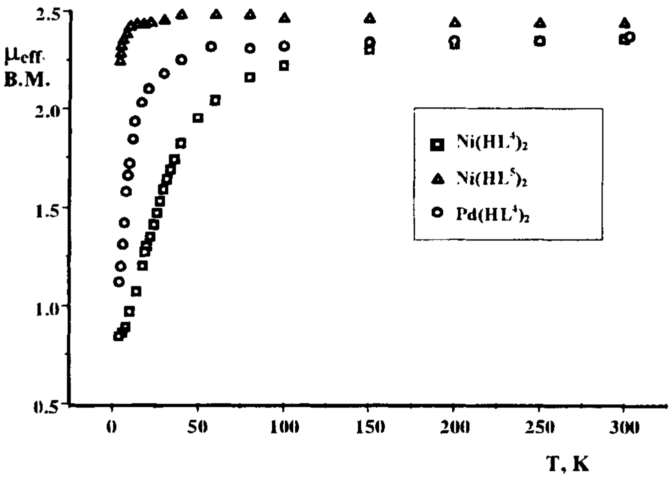


FIGURE 2 μ_{eff} versus T plots for the complexes.

The X-ray diffraction analysis of $Ni(HL^4)_2$ and $Pd(HL^4)_2$ has revealed the parquet-like packing for both complexes. As shown in Figure 3, this structure is accounted for by the fact that each nickel (or palladium) ion "coordinates" the N•-O group oxygens of neighboring bischelate molecules. The short intermolecular distances -•O...M...O•- are responsible for the large exchange interactions in solid $M(HL^4)_2$. An increase in the M...O•- distances in $Pd(HL^4)_2$ as compared to those in $Ni(HL^4)_2$ (3.23 and 2.95 Å, respectively) decreases the exchange interaction energy (-6.5 and -22.3 cm^{-1}, respectively). We failed to grow quality single crystals of $Ni(HL^5)_2$ and $Pd(HL^5)_2$. However, the considerably smaller values of J for $M(HL^5)_2$ as compared to those for $M(HL^4)_2$ suggest that the substitution of a methyl group of H_2L^4 by the phenyl one (H_2L^5) significantly increases the M...O•- distances in solid $M(HL^5)_2$.

In the above discussion of the structures of $Ni(HL^4)_2$ and $Pd(HL^4)_2$, we mentioned that the nickel or palladium ion "coordinates" the oxygen atoms of N•-O groups. We did it because it is evident that at the given distances the chemical bond is not formed. Otherwise, in $Ni(HL^4)_2$, the high-spin ion of Ni(II) would have an octahedral environment. In fact, the structures of $Ni(HL^4)_2$ and $Pd(HL^4)_2$ clearly demonstrate the efficiency of spin interactions through the diamagnetic metal ion. With the diamagnetic metal ion absent, the exchange interactions between the unpaired electrons of N•-O groups separated by 6 Å would be no more than 1 cm^{-1}.[1,3] In our case, in the exchange cluster N•-O...Ni(II)...O-•N, these interactions reach 22.3 cm^{-1}. The Ni(II) ion acts as a bridge that conducts the exchange interactions. This clarifies the nature of the antiferro-

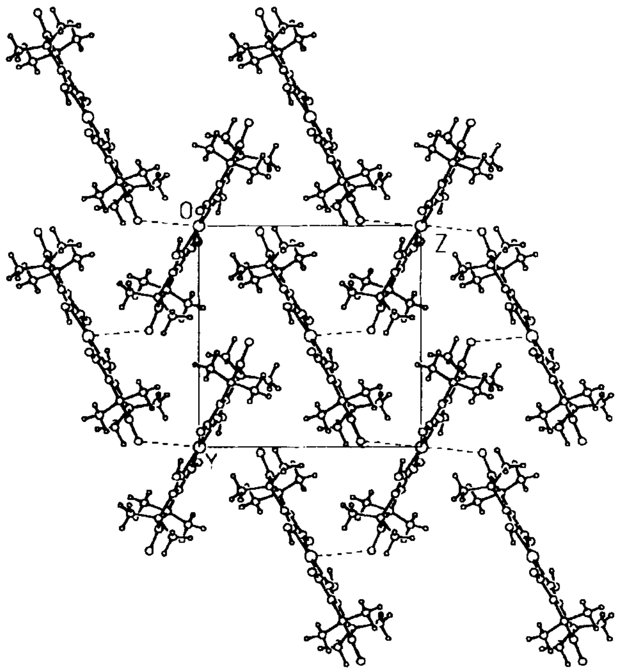
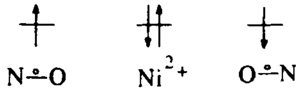


FIGURE 3 Packing of the $M(HL^4)_2$ molecules.

magnetic interaction of N•-O group spins, which occurs by the spin polarization mechanism:

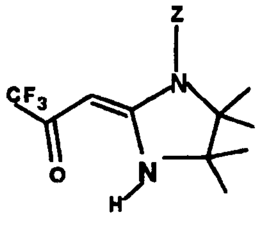


Thus, the investigation of Ni(II) and Pd(II) complexes with HL^4 and HL^5 has revealed a significant influence of the steric availability of the nitroxyl group on the magnetic properties of the complexes in solid. It is noteworthy as well that studying the magnetic properties of solid $Ni(HL^4)_2$ and $Pd(HL^4)_2$ we established the high efficiency of the bridging diamagnetic metal ion in the "conduction" of exchange interactions.

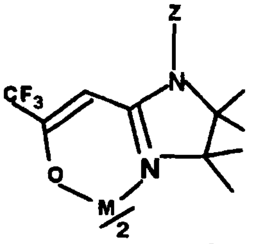
THIRD PAIR

Change in chemical behavior

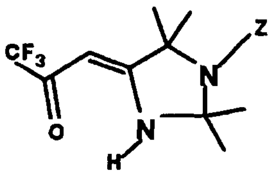
In this section we compare the chemical behaviors of the structural isomers HL^8 and HL^{10} The reaction between enamineketone HL^{10} and metal ions in water-alcohol mixture yields stable bischelates $M(L^{10})_2$.[3,4,6,9] However, HL^8 itself is absolutely unstable. In solution, it is stable only during a few minutes. The reason is the presence of the acid hydrogen atom of the enamineketone functional group near the N•-O group. Thus, the synthesis procedure used for $M(L^{10})_2$ was inapplicable to the synthesis of $M(L^8)_2$ by the same way like In this case, we had to previously synthesize and investigate the metal complexes with the diamagnetic precursors of the paramagnetic enamineketone $M(L^6)_2$ and $M(L^7)_2$.



Z = H (HL^6)
Z = OH (HL^7)
Z = •O (HL^8)



Z = H ($M(L^6)_2$)
Z = OH($M(L^7)_2$)
Z = •O($M(L^8)_2$)



Z = OH (HL^9)
Z = •O(HL^{10})

Earlier we synthesized metal complexes with the hydroxylamine derivative HL^9 in the same manner as the complexes with the stable nitroxide HL^{10} without special precaution.[10] However, the chemical behavior of $M(L^n)_2$, where n = 6-8, significantly differs from that of $M(L^9)_2$ or $M(L^{10})_2$. All $M(L^n)_2$ complexes, where n = 6-8, are thermally unstable and sensitive to hydrolysis. As a consequence, the synthesis of these bischelates should be carried out in anhydrous solvents, where $M(L^6)_2$, $M(L^7)_2$, and $M(L^8)_2$ are stable for a long time (sometimes for months). In $M(L^n)_2$ (n = 6-8), steric hindrances appear to be considerably stronger than those in $M(L^n)_2$ (n = 9,10). A change in the position of the N•-O group in the imidazolidine heterocycle (or in the position of the side chain) results in the formation of a $M(L^n)_2$ (n = 6-8) that is less stable than $M(L^n)_2$ (n = 9, 10). Most structurally characterised metal bischelate molecules with deprotonated 3-imidazoline enamineketone derivatives have almost planar structures.[3,4,6,9] The structure of $M(L^6)_2$, where M = Ni, Co, Cu, Pd, and $Ni(L^7)_2$, significantly deviates from planar. As can be seen from some selected data given in Table 1 all these molecules in solid are essentially nonplanar. This can be responsible for the difficult oxidation of $M(L^7)_2$ (M = Ni, Co, Cu, Pd) compared to $M(L^8)_2$. For example, only 90% of $Pd(L^7)_2$ is oxidized by PbO_2 in pure ethylacetate for 2 hours at room temperature. The oxidation of $M(L^9)_2$ in $M(L^{10})_2$ under the same conditions proceeds quickly and quantitatively. This suggests that the transformation of $M(L^9)_2$ to $M(L^{10})_2$ requires considerable structural rearrangements of the bischelate molecules.

As one could expect,[1] in $M(L^8)_2$, the energies of the exchange interactions between unpaired electrons are higher than those in $M(L^{10})_2$ (of the order of 100 cm^{-1}), which is a consequence of the changed position of the double bond in the bischelate molecule. Thus, the isomers HL^8 and HL^{10}, bearing different substituents in the α-position to the nitroxyl group, show different chemical behaviors, and their metal bischelates possess noticeably different magnetic properties.

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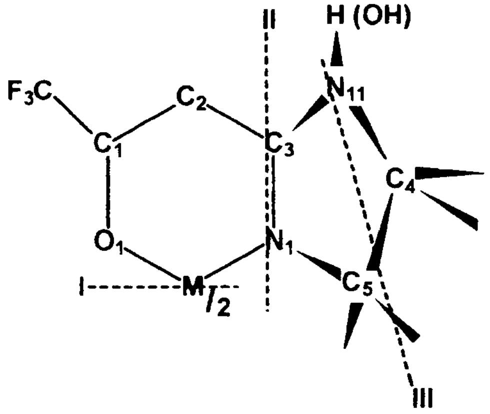

Table 1 Selected bond lengths (Å) and angles in $M(L^n)_2$ molecules.

ML_2	CuL^6_2		NiL^6_2	PdL^6_2	NiL^7_2
M-O1	1.926(4)	1.961(5)	1.953(2)	2.006(2)	1.926(2)
M-N1	1.952(6)	1.912(7)	1.937(2)	2.046(2)	1.941(2)
∠O1MN1	97.6(2)	95.3(2)	93.85(9)	89.07(8)	93.3(1)
O1-C1	1.28(1)	1.26(1)	1.302(3)	1.308(3)	1.288(4)
N1-C3	1.30(1)	1.28(1)	1.305(4)	1.306(3)	1.303(4)
C1-C2	1.38(1)	1.36(1)	1.349(4)	1.333(4)	1.354(5)
C2-C3	1.417(7)	1.441(10)	1.442(4)	1.434(4)	1.423(5)
C3-N11	1.397(10)	1.368(11)	1.344(4)	1.362(3)	1.409(4)
N11-C4	1.507(7)	1.496(10)	1.480(4)	1.473(4)	1.498(4)
N11-H11 (O11)	-		0.70(4)	0.71(3)	1.428(3)
C4-C5	1.56(1)	1.54(1)	1.568(4)	1.567(3)	1.560(5)
C5-N1	1.520(6)	1.497(8)	1.494(4)	1.505(3)	1.494(4)
∠C3N11H11 (O11)	-		116(6)	121(2)	113.7(3)
∠C4N11H11 (O11)	-		121(3)	113(2)	113.5(2)
∠C3N11C4	112.8(6)	108.4(6)	109.0(2)	108.3(2)	105.3(2)
∠I	124.7		92.8	180.0	106.5
∠II	16.4	5.8	4.2	13.3	6.5
∠III	26.7	29.1	27.2	29.4	36.6

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