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New method for the synthesis of heterospin metal complexes with nitroxides

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A new approach was developed to synthesize transition metal complexes with nitroxides based on the simultaneous involvement of nitronyl nitroxide and imino nitroxide in the reaction with metal. It was shown that the reaction of a metal with nitronyl nitroxide can afford a metal complex containing two different radicals in the metal coordination sphere in the case when imino nitroxide is generated in the reaction medium *via* a redox process. The reaction of a metal with imino nitroxide also can give mixed-ligand complexes, in which the metal coordinates both the starting imino nitroxide and its reduction product — the corresponding amidine oxide. This compound can be prepared by an alternative synthesis using the reaction of metal with sterically hindered amidine oxide, resulting in the formation of mixed-ligand coordination compounds through the coordination of both the starting amidine oxide and its oxidation product — imino nitroxide. In the latter case, the following conditions have to be met: the reaction should be performed in the presence of oxygen and transition metal, which can easily change its oxidation state under ambient conditions (Co^{II}, Mn^{II}, Fe^{II}). To synthesize mixed-ligand complexes with transition metals that are not prone to change the oxidation state under ambient conditions (Ni^{II}, Zn^{II}), a specially prepared mixture of nitronyl nitroxide and imino nitroxide should be added to the reaction mixture. It is worth noting that the reaction can be performed using nitronyl nitroxide and imino nitroxide belonging to different series, which significantly extends the scope of the method.
The bibliography includes 156 references.

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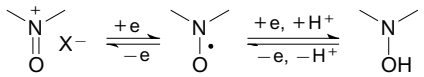
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1. Introduction

Stable organic radicals are extensively used in fundamental and applied research.[1,2] Of particular importance are nitroxides as kinetically most stable paramagnetic organic compounds.[3–5] Due to high sensitivity of their magnetic properties to changes in the local environment and intramolecular effects, nitroxides are attractive tools in biochemistry, biophysics and materials science.[6–12] These compounds can be applied in the controlled polymerization.[3–18] They are promising contrast agents for magnetic resonance imaging[19–24] and are utilized in organic rechargeable battaries[25–34] and as components of metal-air and solar cells.[35–41] Nitroxides are commonly used as organic paramagnetic building blocks in the synthesis of heterospin molecular magnets.[42–51] Transition metal complexes with nitroxides were employed to design single-molecule magnets and breathing crystals.[6,52,53]

Nitroxides can exist in the kinetically stable one-electron reduced state (the corresponding hydroxylamine or amidine oxide anion) and the one-electron oxidized state (the oxoammonium cation) (Scheme 1). Hence, nitroxides are in demand for the fabrication of ambipolar redox-active materials utilized in redox-flow batteries for safe energy storage because, in an uncharged state, the cathode and anode compartments in these batteries contain the same substance.[54–57] Redox reactions of organic compounds in the presence of transition metals with organic ligands are of

Scheme 1



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great interest in the development of new catalytic systems.[6, 58 – 73] These reactions have attracted considerable attention as a tool for the design of molecular switches [74 – 81] and as a basis of many biochemical processes.[82, 83] Redox processes are often employed to develop methods for the synthesis of molecular magnets.[63, 84 – 107]

It is worth noting that redox reactions of nitroxides with transition metals give diverse unexpected compounds. Thus, it was shown that the radical can be reduced to form co-crystals of nitroxide and a complex with the corresponding nitrone.[108] In the products isolated by Burdukov *et al.*,[109] a metal ion was reduced with amidine oxide, with the latter being oxidized to the corresponding nitroxide. Redox reactions of metals with dinitroxides can afford complexes in which only one nitroxide group is transformed into a hydroxylamine anion.[110, 111] The oxidation of transition metal coupled with the reduction of coordinated nitroxide was reported.[112 – 114] The formation of a complex containing coordinated nitroxide and its reduction product was detected.[115] Polynuclear complexes were found to catalyze a profound structural transformation of nitroxide molecules.[116] Therefore, the gradually accumulated synthetic material showed that redox transformations involved in the reactions of nitroxides with transition metals can be accompanied by both the expected and specific, in particular rather deep, structural changes of the starting paramagnetic organic compound and changes in the structure and properties of the resulting complex. Therefore, the outcome of the synthesis is often unpredictable, which was repeatedly mentioned by researchers.[117]

Recently, we demonstrated that, despite various complications associated with redox reactions between nitroxides and metal ions, these processes can be used for the synthesis of particular multispin compounds. In this review, the available experimental data are considered in general terms. The factors that play a key role in redox reactions are discusses and an efficient way of eliminating these reactions is proposed. A new method, which we have developed for the synthesis of multispin compounds, is described in detail. This method is based on the simultaneous introduction of two nitroxides in different oxidation states. Emphasis is given to heterospin complexes, which cannot be prepared by alternative methods. It is worth noting that the nitroxides used in the reaction may differ not only in the oxidation state but also in the set of substituents, *i.e.*, may belong to different structural series. The latter means that this method allows the synthesis of a great diversity of heterospin complexes.

To complete the Introduction, let us mention that kinetically stable organic radicals are a huge class of organic compounds capable of participating in various redox processes when reacting with transition metal ions. Very interesting metal complexes with phenoxides, semiquinolates, verdazyls and other organic radicals [118 – 143] are beyond the scope of this review. Here we discuss a special class of redox reactions involving nitroxides, which served as the basis for the development of a new method for the synthesis of heterospin transition metal complexes. Figure 1 presents the formulas of the nitroxides and their diamagnetic analogues discussed in the review.

The following abbreviations are used in the review:

Hfa — hexafluoroacetylacetonate,

L^1H — 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl,

L^2H_2 — 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide,

L^3H — 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl,

L^4H — 2-(2-hydroxy-3-methoxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl,

L^5H_2 — 2-(2-hydroxy-3-methoxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide,

L^6H — 2-(2-hydroxy-3-methoxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl,

L^7H — 2-(imidazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl,

L^8H — 2-(imidazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl,

L^9H — 2-(2-hydroxy-3-bromo-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl,

$L^{10}H_2$ — 2-(2-hydroxy-3-bromo-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide,

$L^{11}H$ — 2-(2-hydroxy-3-bromo-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl,

PivH — pivalic acid,

Piv — pivalate anion.

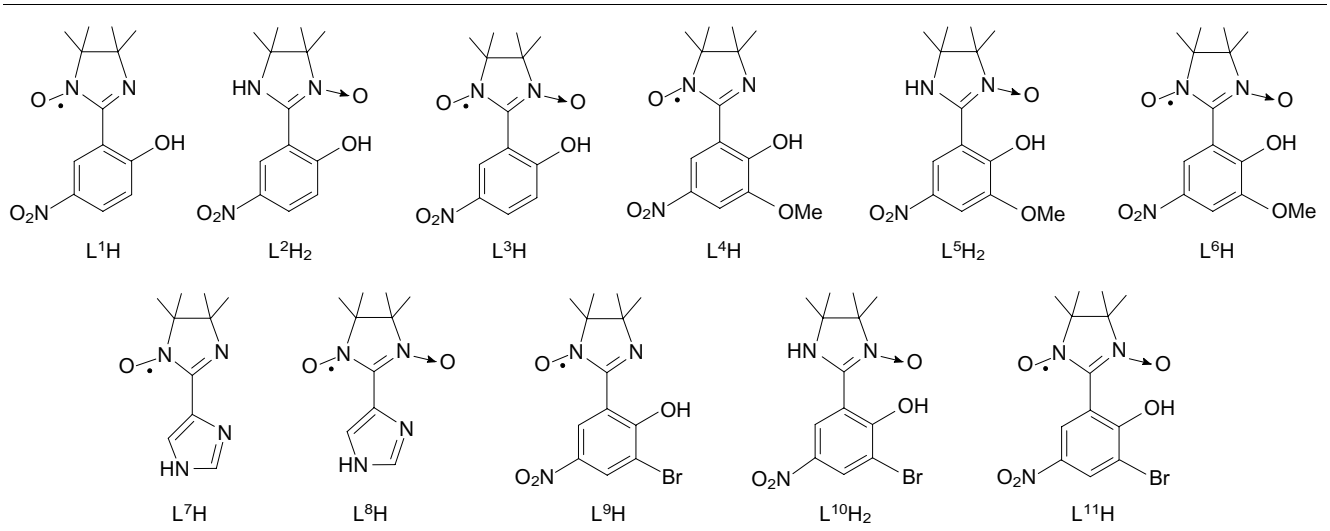


Figure 1. Nitroxides and their diamagnetic analogues.

2. Redox-induced change in the ligand coordination mode

2.1. Development of an approach

A study of the reaction products of cobalt pivalate $[Co_2(Piv)_4(PivH)_4(H_2O)]$ with 2-imidazoline nitroxide L^1H (see Fig. 1) revealed a specific effect, resulting in a redox-induced change in the ligand coordination mode.[144] It was found that the redox process occurs to a significant extent in an acetone/heptane mixture at the reactant ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^1H \sim 1.5-2.5$. Under these conditions, the reaction affords numerous products, including the trinuclear heterospin complex $[Co_3(Piv)_2(L^1)_2(L^2H)_2]\cdot Me_2CO\cdot C_7H_{16}$ (**1**$\cdot Me_2CO\cdot C_7H_{16}$), which was formed in a yield of at most 20%. Nevertheless, compound **1** has attracted considerable attention because it contains the starting L^1 and also L^2H, which was generated *via* the one-electron reduction of nitroxide to the corresponding hydroxylamine, coordinated in the form of a prototropic isomer (nitrone, see Fig. 2). This fact was repeatedly confirmed by X-ray diffraction. Thus, the N–O distance of the nitroxide moiety L^1 significantly differs from that of the nitrone moiety L^2H [1.274(9) and 1.360(8) Å, respectively]. In the case of L^1, these distances are typical of the nitroxide moiety, whereas longer bonds in L^2H are typical of coordinated nitrone.[145] It is worth noting that compound **1** was produced in a narrow range of reactant ratios. At any other reactant ratio or upon the addition of KPiv to a mixture of L^1H and $[Co_2(Piv)_4(PivH)_4(H_2O)]$, the reaction gave $[Co_3(Piv)_4(L^1)_2]$ (**2**), $[Co(L^1)_2]$ (**3**) or $[K_2Co_4(Piv)_8(L^1)_2(PivH)_4]\cdot 2C_7H_{16}$ (**4**$\cdot 2C_7H_{16}$), containing intact L^1, in high yields. Figure 2 presents the molecular structures and the yields of compounds **1** – **4**. It is worth noting that under the conditions of the synthesis of **2** – **4**, products containing the transformed ligand L^1 were not detected.

In the reaction giving **1**, the starting radical serves several functions. A part of L^1H molecules act as a ligand that remains intact, while another part undergoes a redox transformation to L^2H_2. The redox transformation of the ligand is accompanied by a change in its coordination mode. In molecule **1**, the terminal ligands L^1 form six-membered metallocycles typical of Schiff bases, whereas the reduction of L^1H to the corresponding hydroxylamine followed by a prototropic rearrangement to nitrone L^2H_2 leads to the displacement of the imidazoline N atom from the coordination environment of the metal atom and its rotation with respect to the nitrophenol moiety. Hence, L^2H in compound **1** is coordinated *via* oxygen atoms of the nitrone group and the deprotonated phenol moiety, resulting in the formation of a seven-membered metallocycle (see Fig. 2). We called this effect 'a redox-induced change in the ligand coordination mode'.[144] Since this process involves the one-electron reduction of an organic ligand, it was difficult to detect this effect without using a stable radical in the reaction. It should be noted that this result would be useful in the investigation of the functions of biological systems. Thus, there are a plenty of publications dealing with metalloproteins, in which their functions are not fully understood, the investigation of the functions of particular metalloproteins being often complicated by the alteration of the character of their functioning during redox processes.[146]

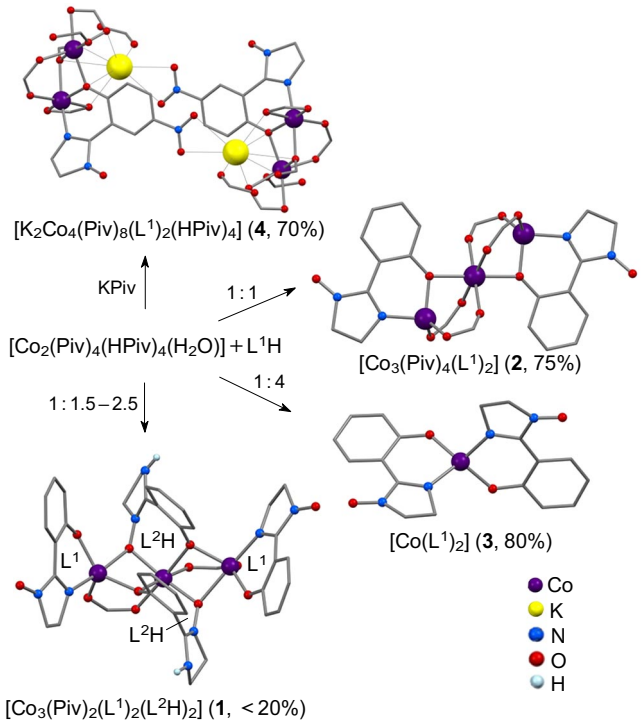


Figure 2. Structures and yields of $[Co_3(Piv)_2(L^1)_2(L^2H)_2]$ (**1**), $[Co_3(Piv)_4(L^1)_2]$ (**2**), $[Co(L^1)_2]$ (**3**) and $[K_2Co_4(Piv)_8(L^1)_2(PivH)_4]$ (**4**). Hereinafter, carbon atoms, methyl and nitro groups are omitted for the sake of clarity. Compiled from Ovcharenko *et al.*[144]

2.2. Factors that favour redox reactions

Since we found a redox-induced change in the ligand coordination mode when studying polynuclear complex **1**, it would be assumed that the reduction of L^1 to L^2H and the formation of a seven-membered metallocycle were due to the fact that L^2H acts as a bridge. However, further studies showed that the reaction can afford mononuclear complexes containing both L^1 and L^2H. In particular, $[Mn(L^1)_2(L^2H)]\cdot Me_2CO$ (**5**$\cdot Me_2CO$), $[Cr(L^1)_2(L^2H)]$ (**6**) and $[Fe(L^1)_2(L^2H)]\cdot Me_2CO$ (**7**$\cdot Me_2CO$) were synthesized and characterized. In these complexes, the metal atoms coordinate two deprotonated imino nitroxide molecules and one deprotonated amidine oxide molecule, which forms a seven-membered ring with the metal. All $[M(L^1)_2(L^2H)]$ are structurally similar. Figure 3 shows the molecular structure of $[Mn(L^1)_2(L^2H)]$, the single crystals of which, like those of the Fe complex, contain an acetone solvent molecule. The coordination environment of manga-

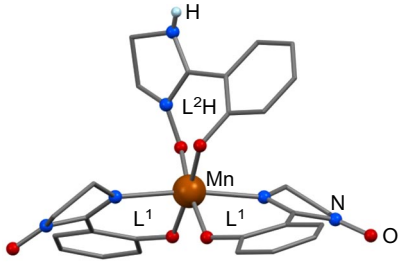


Figure 3. Molecular structure of $[Mn(L^1)_2(L^2H)]$ (**5**). Compiled from Kuznetsova *et al.*[147]

nese can be described as a square bipyramid, with oxygen atoms of the deprotonated phenoxide groups L^1 and the nitrone group L^2H lying in an equatorial plane. These distances are significantly shorter (by ~0.4 Å) than the axial Mn – N distances, where N are nitrogen atoms of imino groups L^2H. An elongation of Mn – N distances is a consequence of the Jahn – Teller distortion typical of Mn(III). The N – O distances in L^1 [1.267(3) and 1.277(3) Å] are typical of nitroxides.[4] The N – O distance in L^2H is significantly longer [1.357(2) Å], which, as mentioned above, is typical of heterocyclic nitrones.

It should be noted that compounds **6** and **7** were synthesized starting from Cr(III) and Fe(III) salts, whereas compound **5** was prepared starting from a Mn(II) compound.[147] In the reaction of L^1H using Ni(II) instead of Mn(II), imino nitroxide is not reduced, resulting in the formation of $[Ni(L^1)_2(H_2O)_2]\cdot 2\,Me_2CO$ (**8**) (Fig. 4). Similarly, the reaction of L^1H with nickel pivalate $[Ni_2(Piv)_4(PivH)_4(H_2O)]$ instead of related $[Co_2(Piv)_4(PivH)_4(H_2O)]$ affords only $[Ni_3(L^1)_2(Piv)_4(PivH)_4]$ (**9**) (see Fig. 4). Hence, it can be concluded that the formation of **1** and **5** – **7** is favoured not only by kinetic stability of L^1 and L^2H but also by the ability of the metal to exist in different oxidation states. It should be noted that the synthesis of **5** produces $[Mn(L^1)_2(L^2H)]$ under an inert atmosphere as well. This is evidence that it is L^1 that oxidizes Mn(II) to Mn(III) under these reaction conditions. The ability of Mn(II) to be oxidized to Mn(III) is a necessary condition for the preparation of **5**.

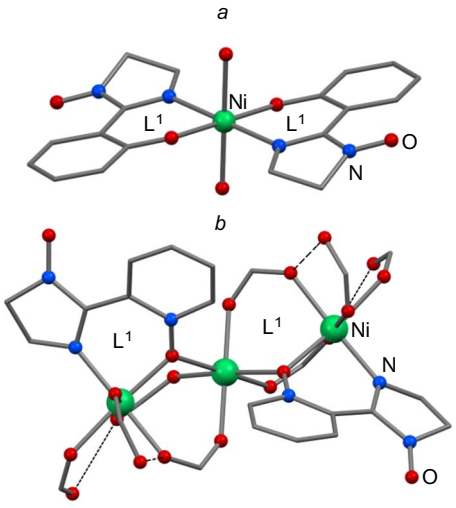


Figure 4. Structures of $[Ni(L^1)_2(H_2O)_2]$ (**8**) (*a*) and $[Ni_3(L^1)_2(Piv)_4(PivH)_4]$ (**9**) (*b*). Compiled from Ovcharenko *et al.*[144] and Kuznetsova *et al.*[147]

As mentioned above, compound **1** is formed as a solid product within a narrow range of reactant ratios and is isolated as the mixed solvate $\mathbf{1}\cdot Me_2CO\cdot C_7H_{16}$. Since the formation of this mixed-ligand complex is accompanied by redox reactions, it is not surprising that the synthesis affords a mixture of products. Hence, it was the luck that crystals of $\mathbf{1}\cdot Me_2CO\cdot C_7H_{16}$, unlike other products, labelled themselves. Being filtered off, these crystals lost solvent molecules within a few minutes and began to crack. This process was accompanied by intense mechanical motion in crystals, which has always attracted considerable attention of researchers. In order to improve the yield of compound **1**, different solvents and their mixtures were utilized for its synthesis and crystallization. The conditions were found for the reproducible synthesis of $\mathbf{1}\cdot 1.5\,Me_2CO$, $\mathbf{1}\cdot 3\,Me_2CO\cdot C_7H_{16}$ and $\mathbf{1}\cdot MeCN$. After the separation of the crystals of $\mathbf{1}\cdot Solv$ from the mother liquor, the character of their chemomechanical activity depended on the set of solvent molecules incorporated in the crystals.[144] However, the nature of the solvent has little effect on the yield of target compound **1**. The yield of this compound was significantly increased by performing the synthesis in the presence of an equimolar mixture of L^1H and authentic L^2H_2. Under these conditions, the redox reaction was suppressed because the synthetic system contained both imino nitroxide and its reduction product in a ratio favourable for the formation of compound **1**. It was shown that a similar approach can be applied to prepare mononuclear complexes. For example, complex **7** is easily formed in the reaction of $FeCl_3$ with two equivalents of L^1H and one equivalent of L^2H_2 in the presence of alkali.

Compound **1** can be synthesized starting only from L^2H_2. However, the presence of air oxygen in the synthetic system is required in this case. Under an inert atmosphere, the reaction does not occur (Fig. 5). Since solutions of L^2H_2 in organic solvents are air-stable over a long period of time, the presence of a transition metal is necessary for initiating the oxidation of L^2H_2 to L^1H with air oxygen.

To conclude this section, note that the simultaneous functioning of the nitroxide – hydroxylamine pair is rather rarely detected by experimental methods.[110 – 115] As specially noted,[117] a few such examples were found unintentionally in an attempt to synthesize transition metal complexes with a nitroxide of a certain structure. Examples of the functioning of the nitroxide – hydroxylamine pair in the absence of transition metals in the reaction mixture are also rare. Thus, an oscillating reaction based on recycling was described for the $(Bu^t)_2N-O^{\bullet}/(Bu^t)_2N-OH$ pair in 1990.[148] This reaction was still not detected in other processes. We believe that the discovered change in the ligand function would occur much more often.

3. Synthesis of mixed-radical complexes

The formation of **1** indicates that there is a special class of metal coordination compounds with nitroxides, in which both the starting radical and its reduction product are involved in the metal coordination environment. This fact, and also the fact that the highest yield of compound **1** was achieved in the reaction with an equimolar mixture of L^1H and L^2H_2, suggested that it would be interesting to simultaneously introduce a mixture of two radicals (L^1H and L^3H) in the reaction with transition metals. In molecule **1**, both iminoxyl radicals form six-membered metallocycles typical of Schiff bases, whereas L^2H are coordinated in a tetradentate-bridging mode so that the 'central' Co atom (hereinafter, the word central enclosed in quotes means that among all the central metal atoms in a polynuclear molecule, this metal atom is at the centre of the molecule or at the centre of the formal chain of metal atoms) forms seven-membered metallocycles with these ligands (Fig. 6 *a*). The L^2H donor group involved in seven-membered metallocycles in the $[Co_3(Piv)_2(L^1)_2(L^2H)_2]$ molecule is identical to that in the nitronyl nitroxide L^3 (Fig. 6 *b*). This gave impetus to a study of the reaction product of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ and an equimolar mixture of L^1H

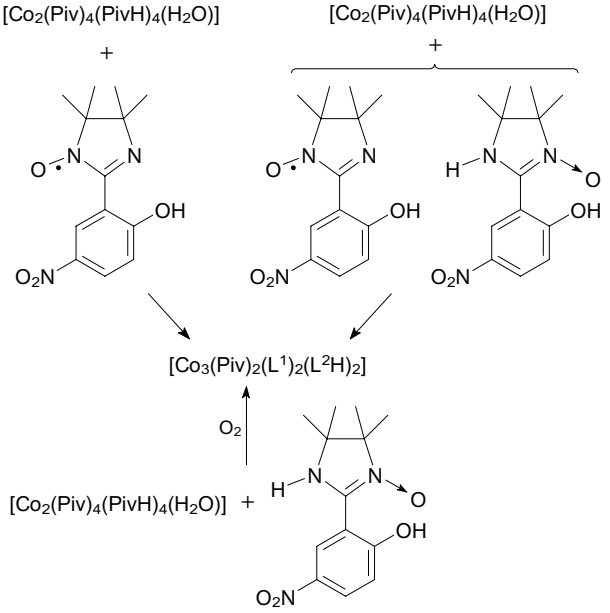


Figure 5. Alternative syntheses of **1**.

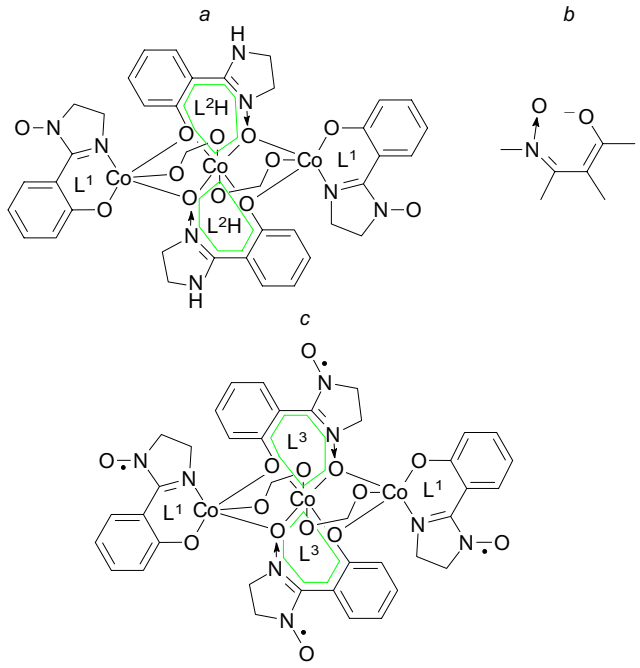


Figure 6. Metallocycles formed by L^1 and L^2H with Co atoms in molecule **1** (*a*); the L^2H donor group and the L^3 group favourable for the formation of seven-membered metallocycles (*b*); the trinuclear molecule $[Co_3(Piv)_2(L^1)_2(L^3)_2]$ (**10**) (*c*).

and L^3H. It was expected that, since the L^2H donor group is isostructural with L^3, it will be favourable for the introduction of L^3 into the complex, giving a multispin complex with two different paramagnetic ligands.

Actually, the reaction of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ with a mixture of nitroxides L^1H and L^3H affords the trinuclear complex $[Co_3(Piv)_2(L^1)_2(L^3)_2]$ (**10**) containing both imino nitroxide and nitronyl nitroxide. The optimal staring reactant ratio is $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^1H : L^3H = 3 : 4 : 4$. It corresponds to the stoichiometric coefficients of reaction (1) giving **10** in a yield of $\geqslant 70\%$.

$$3[Co_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^1H + 4L^3H \rightarrow \quad (1)$$

$$\rightarrow 2[Co_3(Piv)_2(L^1)_2(L^3)_2] + 20\,PivH + 3\,H_2O$$

These coefficients can easily be determined because they are the same as those in the synthesis of **1**. Trinuclear molecule **10** (Fig. 6 *c*), isolated as a solvate with acetone **10** · 2 Me_2CO, is isostructural with molecule **1**. The terminal Co atoms coordinate by imino nitroxides to form six-membered rings. The 'central' Co atom forms seven-membered metallocycles with L^3. Therefore, the reaction of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ with an equimolar mixture of L^1H and L^3H provides a convenient method for the synthesis of a heterospin complex containing two different paramagnetic ligands.

To complete the consideration of this series of reactions, the nature of the product generated in the reaction of Co(II) pivalate with nitronyl nitroxide L^3H was elucidated. Thus, the reaction of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ with L^3H was found to afford the pentanuclear heterospin complex $[Co_5(Piv)_4(L^1)_2(L^3)_4]$ (**11**) as a solid product.[149] Its ligand environment also includes two different radicals — imino nitroxide L^1 and nitronyl nitroxide L^3 (Fig. 7). In this reaction, L^1 is formed *via* a redox process accompanied by deoxygenation of L^3. The complex is always generated in the reaction of Co(II) pivalate with L^3H in an acetone/heptane mixture at $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^3H$ ratios varying from 1 : 1 to 1 : 4; the product was obtained in a good yield (~50% – 60%). However, the highest yield (~70%) of **11**, which formed as the solid solvate **11** · 0.5 Me_2CO · 0.5 C_7H_{16}, was achieved at the reactant molar ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^1H : L^3H = 5 : 4 : 8$. It was difficult to predict this ratio, and it was determined only after the crystal structure determination. This ratio corresponds to the stoichiometric coefficients of the reaction

$$5[Co_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^1H + 8\,L^3H \rightarrow \quad (2)$$

$$\rightarrow 2[Co_5(Piv)_4(L^1)_2(L^3)_4] + 32\,PivH + 5\,H_2O$$

The Co atoms in the pentanuclear molecule have three different coordination modes: tetrahedral for Co2, octahedral for Co1 and Co3 and trigonal-bipyramidal for Co4 and

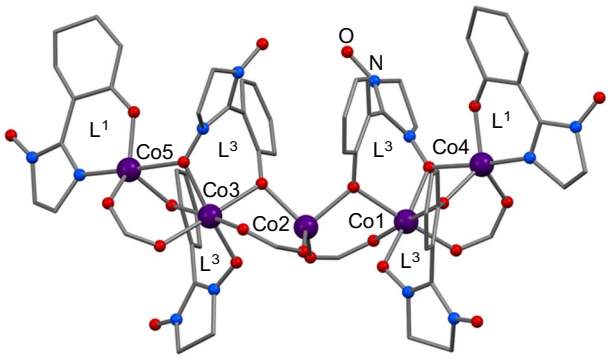


Figure 7. Molecular structure of $[Co_5(Piv)_4(L^1)_2(L^3)_4]$ (**11**). Compiled from Ovcharenko *et al.*[149]

Co5 (see Fig. 7). It is worth noting that polynuclear molecules **10** and **11** contain similar structural moieties. Thus, the coordination environment of the Co4 and Co5 atoms in molecule **11** (see Fig. 7) is identical to that of the terminal Co atoms in molecule **10** (see Fig. 6), and the coordination environment of the Co1 and Co3 atoms in molecule **11** is identical that of the 'central' Co atom in molecule **10**. The terminal cobalt atoms (Co4 and Co5) in molecule **11**, like those in molecule **10**, coordinate imino nitroxides to form six-membered metallocycles typical of Schiff bases, while the Co1 and Co3 atoms form seven-membered metallocycles with nitronyl nitroxides. Hence, it is not surprising that the use of an authentic mixture of L^1H and L^3H in the synthesis often results in the formation of a difficult-to-separate mixture of $\mathbf{11}\cdot 0.5\,Me_2CO\cdot 0.5\,C_7H_{16}$ and $\mathbf{10}\cdot 2\,Me_2CO$. Nevertheless, the utilization of the reactants in a ratio of 3 : 4 : 4 resulted in the crystallization of trinuclear complex **10**, whereas pentanuclear complex **11** was generated as a single or major product in the reaction using reactants in a ratio of 5 : 4 : 8.

As mentioned above, imino nitroxide remains intact in the reaction of L^1H with $[Ni_2(Piv)_4(PivH)_4(H_2O)]$. Similarly, no redox transformations of the radical were observed in the reaction of Ni(II) pivalate with nitronyl nitroxide L^3H. Moreover, regardless of the initial reactant ratio and reaction conditions, no products of the reaction between Ni(II) pivalate and L^3H were isolated. Thus, the starting L^3H precipitated as the solid product after concentrating the solution. On the contrary, the simultaneous introduction of L^1H and L^3H in the reaction resulted in the formation of the mixed-radical complex $[Ni_3(Piv)_3(L^1)_2(L^3)(PivH)_3]$ (**12**). The highest yield of **12** (~60%) was achieved at the reactant ratio $[Ni_2(Piv)_4(PivH)_4(H_2O)] : L^1H : L^3H = 3 : 4 : 2$ corresponding to the stoichiometric coefficients of the reaction

$$3[Ni_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^1H + 2\,L^3H \rightarrow \quad (3)$$

$$\rightarrow 2[Ni_3(Piv)_3(L^1)_2(L^3)(PivH)_3] + 12\,PivH + 3\,H_2O$$

In molecule **12**, the Ni atoms have an octahedral coordination environment and all paramagnetic ligands adopt a tridentate bridging-chelating mode. Each PivH molecule, coordinated in a monodentate mode, forms a hydrogen bond with one O atom of the adjacent μ_2-O,O′-pivalate anion (Fig. 8). Hence, despite the same nuclearity, the composition and structure of **12** significantly differ from those of **10** (see Figs. 6 and 8).

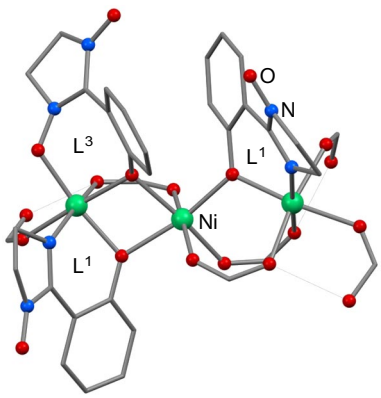


Figure 8. Molecular structure of $[Ni_3(Piv)_3(L^1)_2(L^3)(PivH)_3]$ (**12**). Compiled from Ovcharenko *et al.*[149]

Therefore, taking into account the fact that nitronyl nitroxide, appropriate imino nitroxide and the corresponding nitrone are often kinetically stable compounds and can be isolated in individual state, the synthesis can be accomplished using an authentic mixture of components, as in the synthesis of **1** and **10** – **12**. This is particularly important for **12**. Since Ni(II) pivalate does not initiate the transformation of nitronyl nitroxide into imino nitroxide, compound **12** cannot be synthesized in alternative ways, *i.e.*, without the simultaneous addition of L^1H and L^3H to the reaction mixture. The simultaneous introduction of nitronyl nitroxide and imino nitroxide or a mixture of imino nitroxide and the appropriate nitrone in the reaction with transition metal underlies the method for the synthesis of heterospin complexes. The nitronyl nitroxide – imino nitroxide pair (or the imino nitroxide – amidine oxide pair) can be prepared at any reactant ratio. This is essential because it is difficult to predict the stoichiometric ratio of the components in the resulting mixed-ligand complex. However, in the case when single crystals of the new compounds can be obtained, the ratio of the components can be determined and used for the subsequent preparation of the target product. This approach allows the synthesis of heterospin complexes in high yields.

It should be noted that multispin molecules prepared by this method contain a complex system of exchange channels, which requires an additional study in each case. Since this review is focused solely on the new synthetic approach to the preparation of heterospin metal complexes with nitroxides, the magnetic properties of the resulting compounds are not discussed. Note that this method can be applied to prepare both heterospin molecular magnets and single-molecule magnets.[149]

4. Extension of the synthetic potential

4.1. Simultaneous introduction of two nitroxides of different series in the reaction

The approach based on the simultaneous introduction of nitronyl nitroxide and imino nitroxide in the reaction with metals was shown to have a broad synthetic scope. Heterospin complexes containing different paramagnetic ligands in the coordination environment can be synthesized by simultaneously using nitronyl nitroxides and imino nitroxides, which differ by the substituents, *e.g.*, L^1H and L^6H or L^3H and L^4H (see Fig. 1). Due to the importance of steric complementarity, the synthesis of a heterospin complex containing different paramagnetic ligands may require the use of nitronyl nitroxide and imino nitroxide of another series, *i.e.*, of imino nitroxide, which is not a reduction product of the nitronyl nitroxide utilized in the reaction.

As can be seen in Fig. 1, $L^4H - L^6H$ differ from $L^1H - L^3H$ only by the presence of a methoxy substituent in the phenyl ring. Hence, it would be expected that these groups of ligands will differ only slightly in the functionality, *i.e.*, the reactions of $L^4H - L^6H$ with binuclear Co(II) and Ni(II) pivalates should be similar to those with $L^1H - L^3H$ and afford related products. There is some evidence in favour of this assumption. Thus, the reaction of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ with imino nitroxide L^4H in an acetone – heptane mixture gives solid $[Co_3(Piv)_4(L^4)_2(PivH)_2(H_2O)_2]\cdot C_7H_{16}$ ($\mathbf{13}\cdot C_7H_{16}$) at the reactant ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^4H = 1 : 1 - 1 : 2$

and affords $[Co(L^4)_2(PivH)_2]$ (**14**) as the major product at reactant ratios varying from 1 : 4 to 1 : 6. Complex **14** can be prepared in pure form in high yield from a CH_2Cl_2 – heptane mixture; the highest yield of **13**·C_7H_{16} was achieved at the reactant ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^4H = 3 : 4$, which is consistent with the stoichiometric coefficients of the reaction

$$3[Co_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^4H + H_2O \rightarrow \quad (4)$$

$$\rightarrow 2[Co_3(Piv)_4(L^4)_2(PivH)_2(H_2O)_2] + 12\,PivH$$

As can be seen in Fig. 9, molecules **13** and **14** contain imino nitroxide L^4, which remains intact in the course of the reaction.

Within the framework of this review, a complex containing both the starting imino nitroxide and its reduction product is of most interest. The synthesis in an acetone/heptane mixture at the reactant ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^4H \geqslant 1 : 4$ can be accompanied by the formation of the complex $[Co_3(L^4)_2(L^5H)_2(Piv)_2]\cdot Me_2CO\cdot H_2O$ (**15**·$Me_2CO\cdot H_2O$) as an admixture to **14**. It should be noted that single crystals of **15**·$Me_2CO\cdot H_2O$ were of very poor quality and the crystal structure was determined with an unreasonably high R factor. However, **15** was easily prepared by the addition of $[Co_2(Piv)_4(PivH)_4(H_2O)]$ to a mixture of L^4H and L^5H_2. In the latter case, the reaction gave **15**·$Me_2CO\cdot H_2O$ as a single solid product in ~45% yield. Acetonitrile proved to be the solvent of choice for the synthesis of **15**. In this case, high-quality single crystals of **15**·1.5 MeCN were obtained. The highest yield (75%) of this compound was achieved at the reactant molar ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : HL^4 : L^5H_2 = 3 : 4 : 4$ corresponding to the stoichiometric coefficients of the reaction

$$3[Co_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^4H + 4\,L^5H_2 = \quad (5)$$

$$= 2[Co_3(L^4)_2(L^5H)_2(Piv)_2] + 20\,PivH + 3\,H_2O$$

The structure of trinuclear molecule **15** is shown in Fig. 9. The terminal nitroxide molecules L^4 are coordinated in a bidentate fashion through the imine N atom and the O atom of the deprotonated phenol group. The deprotonated amidine oxide molecules L^5H, like L^2H in **1** (see Fig. 2), are coordinated in a tetradentate-bridging manner, each phenol O atom and each O atom of the nitrone group being involved in the coordination to two Co atoms. These ligands form seven-membered metallocycles with the 'central' Co atom. The N – O distances in the nitroxide L^4 [1.255(6) – 1.282(9) Å] are significantly shorter than those in the N-oxide group of L^5H [1.322(5) – 1.353(5) Å]. As mentioned in Section 2.2, the change in the function of the paramagnetic ligand should be observed rather often in reactions of organic radicals with transition metals capable of changing the oxidation state. This is vividly confirmed by the formation of **15**.

The reaction of Co(II) pivalate with an equimolar mixture of nitroxides L^6H and L^4H, as in the case of **10**, affords the mixed-radical complex $[Co_3(Piv)_2(L^4)_2(L^6)_2]\cdot 4\,MePh$ (**16**·4 MePh). Complex **16** can be synthesized in high yield (~70%) using the reactant molar ratio $[Co_2(Piv)_4(PivH)_4(H_2O)] : L^4H : L^6H = 3 : 4 : 4$ corresponding to the stoichiometric coefficients of the reaction

$$3[Co_2(Piv)_4(PivH)_4(H_2O)] + 4\,L^4H + 4\,L^6H = \quad (6)$$

$$= 2[Co_3(Piv)_2(L^4)_2(L^6)_2] + 20\,PivH + 3\,H_2O$$

The topology of trinuclear complex **16** is similar to that of molecule **15** (Figs. 9 and 10, respectively). The Co atoms coordinate imino nitroxides L^4 to form six-membered metallocycles, whereas the 'central' Co atom is involved in seven-membered metallocycles with nitronyl nitroxides L^6, which are coordinated in a tetradentate bridging-chelating fashion. The coordination environment of the 'central' Co atom can be described as a distorted octahedron, whereas the environment of the other Co atoms is nearly square pyramidal, with the O_{Piv} atom being at the apex. The oxygen atoms of MeO groups are not coordinated. The N – O interatomic distances in the uncoordinated groups are substantially shorter [1.250(4) – 1.264(4) Å] than those in the coordinated groups containing bridging O atoms [1.325(3) and 1.309(3) Å]. Therefore, the reaction of Co(II) pivalate with a mixture of nitronyl and imino nitroxides provides a convenient approach to the synthesis of heterospin complex **16** containing two different paramagnetic ligands.

Since the oxidation state of Ni(II) remains unchanged in the reactions with nitroxides, the difference in the composition of the products is mainly determined by the ratio of the starting reactants and solubility of the reaction products. At the ratio $[Ni_2(Piv)_4(PivH)_4(H_2O)] : L^4H = 1 : 1$, the trinu-

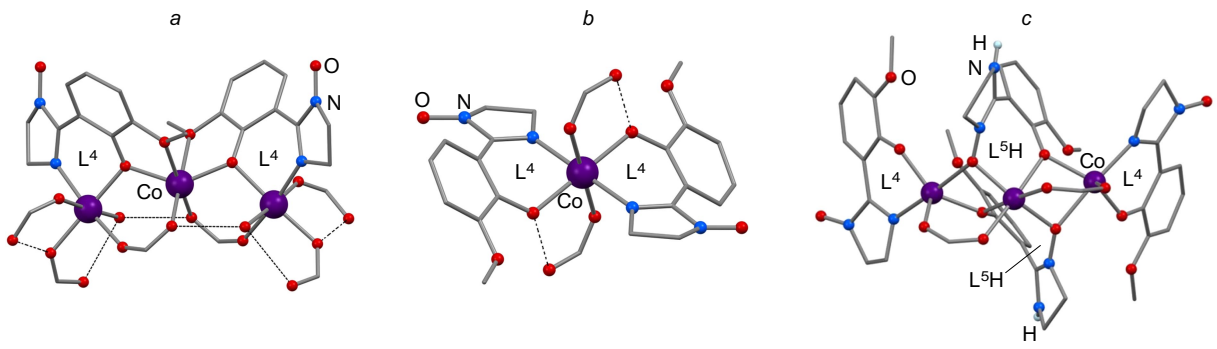


Figure 9. Molecular structures of $[Co_3(L^4)_2(Piv)_4(PivH)_2(H_2O)_2]$ (**13**) (*a*), $[Co(L^4)_2(PivH)_2]$ (**14**) (*b*) and $[Co_3(L^4)_2(L^5H)_2(Piv)_2]$ **15** (*c*). Compiled from Ovcharenko *et al.*[150]

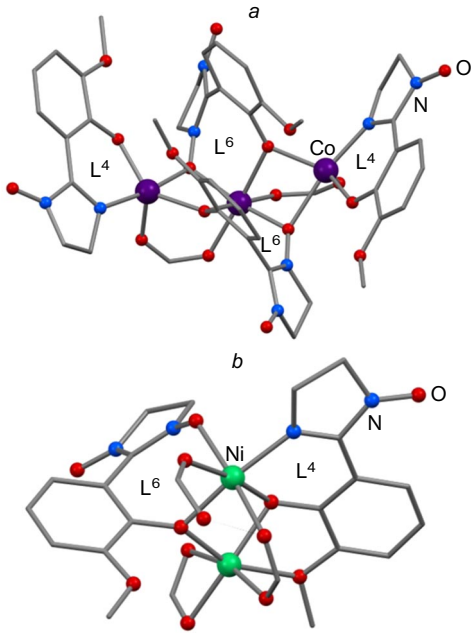


Figure 10. Molecular structures of $[Co_3(Piv)_2(L^4)_2(L^6)_2]$ (**16**) (*a*) and $[Ni_2(Piv)_2(L^4)(L^6)(PivH)]$ (**19**) (*b*). Compiled from Ovcharenko *et al.*[150]

clear complex $[Ni_3(L^4)_2(Piv)_4(PivH)_2(H_2O)_2]\cdot 0.5C_7H_{16}$ (**17**$\cdot 0.5C_7H_{16}$) is formed as the solid product; at a ratio of 1 : 4, the mononuclear complex $[Ni(L^4)_2(PivH)_2]$ (**18**) is generated. The molecular structures of **17** and **18** are almost identical to those of **13** and **14** (Fig. 9), respectively. The only small difference is that **18** can be synthesized as both *trans* and *cis* isomers.[150] Like **10**–**12**, the mixed-radical complex $[Ni_2(Piv)_2(L^4)(L^6)(PivH)]\cdot C_7H_{16}$ (**19**$\cdot C_7H_{16}$) can easily be prepared by the simultaneous introduction of authentic L^4H and L^6H in the reaction. The latter complex cannot be synthesized by alternative methods. The structure of dinuclear molecule **19** is presented in Fig. 10. A comparison of mixed-radical complexes **16** and **19** shows that they are structurally different. In molecule **19**, the Piv anions and PivH feature different structural functions. The paramagnetic ligands are coordinated in different fashion. Thus, the O atom of the MeO group of L^4 is involved in the coordination to the metal, whereas the corresponding O atom of L^6 remains uncoordinated.

The successful synthesis of mixed-radical complexes **10**–**12**, **16** and **19** has stimulated us to study the possibility of performing reactions of metals with mixtures of radicals belonging to different series, *i.e.*, radicals containing different sets of substituents, instead of mixtures of a nitronyl nitroxide and an imino nitroxide belonging to the same series. The existence of such mixed-radical complexes was not evident. Moreover, opposite results would be expected. A complex with a particular ligand is generally precipitated as the solid product from the reaction solution. This serves as the basis for the purification of compounds by crystallization. Complexes with a ligand having a higher binding constant are generally crystallized from a solution since the solubility limit of these complexes is first reached. Besides, complexes with one and the same ligand form more 'symmetric molecules', providing a closer packing of the solid phase. However, the experimental data demonstrated that the formation of mixed-radical Co and Ni complexes is possible. The heteroligand mixed-radical complexes $[Ni_2(Piv)(L^3)(L^4)_2(MeOH)]$ (**20**), $[Co_2(Piv)(L^3)(L^4)_2(MeOH)]$ (**21**), $[Ni_2(Piv)(L^1)(L^6)_2(H_2O)]$ (**22**) and $[Co_3(Piv)_2(L^1)_2(L^6)_2]$ (**23**) can be prepared in high yields (70% – 95%) by the reaction of Ni or Co pivalate with a mixture of two radicals of different series, *e.g.*, nitronyl nitroxide L^3H and imino nitroxide L^4H or nitronyl nitroxide L^6H and imino nitroxide L^1H.[150]

The structures of the mixed-radical Ni and Co complexes are shown in Figs 11 and 12 for the sake of convenience of the pairwise comparison. Dinuclear molecules **20** and **21** are structurally similar. One L^4 ligand is coordinated in a bidentate fashion to form a six-membered metallocycle with the metal, while L^3 is coordinated in a tridentate bridging-chelating mode. The second L^4 is coordinated to the metal ion through the MeO group, thereby making it impossible to form a trinuclear complex similar to **16**, which contains uncoordinated MeO groups.

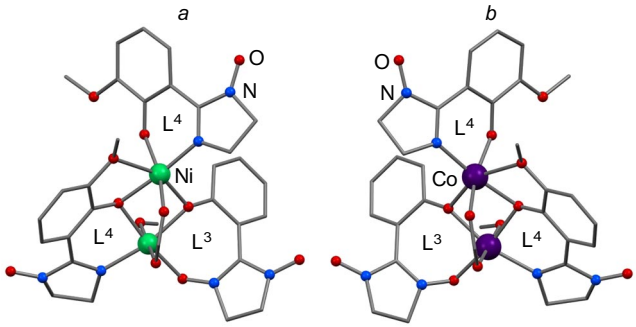


Figure 11. Molecular structures of $[Ni_2(Piv)(L^3)(L^4)_2(MeOH)]$ (**20**) (*a*) and $[Co_2(Piv)(L^3)(L^4)_2(MeOH)]$ (**21**) (*b*). Compiled from Ovcharenko *et al.*[150]

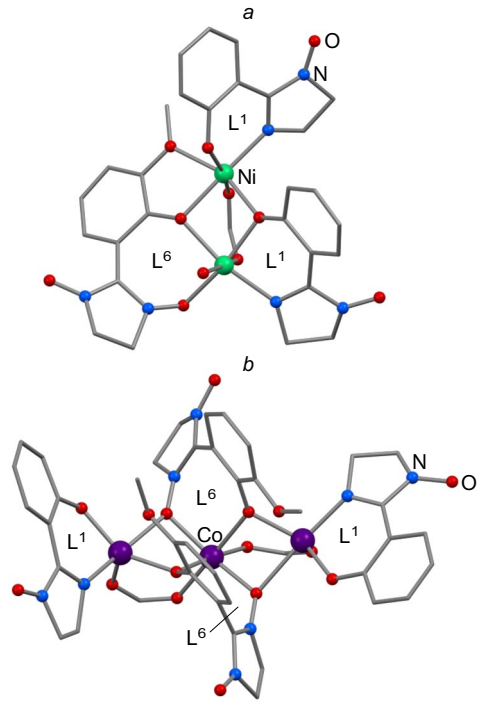


Figure 12. Molecular structures of $[Ni_2(Piv)(L^1)(L^6)_2(H_2O)]$ (**22**) (*a*) and $[Co_3(Piv)_2(L^1)_2(L^6)_2]$ (**23**) (*b*). Compiled from Ovcharenko *et al.*[150]

The molecular structure of **22** is similar to those of **20** and **21** with the difference that L^6 and L^1 in **22** serve the structural functions that were performed by L^3 and L^4, respectively, in **20** and **21**. Trinuclear molecule **23** is structurally similar to **16**. The most significant difference is that L^1 in **23** performs the same function as L^4 in molecule **16**.

Therefore, the simultaneous introduction of nitronyl nitroxide and imino nitroxide, which differ by a set of substituents, in the reaction with a metal is a way to greatly extend the range of available mixed-radical complexes. During the 50-year history of investigation of heterospin transition metal complexes with nitronyl nitroxides and imino nitroxides, thousands of compounds were synthesized and characterized. However, researchers always preferred to perform reactions of metals with either an individual nitronyl nitroxide or an individual imino nitroxide, because the radical-containing reaction mixture often gives several different compounds or a single compound but as several polymorphs; in some cases both processes, simultaneously take place.[1, 107, 151]

Mixtures of paramagnetic ligands were rarely used in reactions with metals, among other reasons, because the synthesis of such compounds is generally followed by investigation of their magnetic properties, which is often performed on a SQUID magnetometer highly sensitive to magnetically active impurities. For this reason, in order to avoid additional synthetic and magnetochemical complications, reactions are generally performed using high-purity individual nitronyl nitroxide or imino nitroxide. The synthetic approach under consideration can be employed in the following way. After the preparation and isolation of a particular transition metal complex with the newly synthesized nitronyl nitroxide or its imino nitroxide analogue, it makes sense to investigate the possibility of the formation of mixed-radical complexes, *i.e.*, such complexes that can be generated in the case of the simultaneous presence of nitronyl nitroxide and imino nitroxide in the reaction mixture. This is a special class of multispin compounds. Combinations of the newly synthesized nitronyl nitroxide (imino nitroxide) and known imino nitroxides (nitronyl nitroxides) greatly increase the number of new multispin compounds. Potentially, the number of such compounds can be very large.

4.2. Derivatives with a heterocyclic substituent in a side chain

For the sake of convenience of the discussion, the possibility of the simultaneous use of nitronyl nitroxide and imino nitroxide in the reaction with transition metals was demonstrated in relation to pairs of paramagnetic Schiff bases, in which a radical molecule contains a phenoxide substituent in a side chain. The question is whether it is possible to extend the range of nitroxide derivatives utilized in the synthesis of mixed-radical transition metal complexes. Nitronyl nitroxides and imino nitroxides containing a heterocyclic substituent in the side chain are the most representative derivatives.[4, 152, 153] This fact stimulated the investigation of the possibility of preparing mixed-radical complexes with imidazole-containing imino nitroxide L^7H and nitronyl nitroxide L^8H. Besides, L^7H and L^8H are soluble and kinetically stable in aqueous solutions, due to which the possibility of performing such reactions can be examined not only in organic media but also in water. The structures of the complexes $[Ni(L^7H)_2(L^8H)](NO_3)_2 \cdot 1.5\,H_2O$ (**24** $\cdot 1.5\,H_2O$) and $[Zn(L^7H)_2(L^8H)](NO_3)_2 \cdot H_2O$ (**25** $\cdot H_2O$), which were prepared by the reaction of Ni(II) and Zn(II) nitrates with L^7H and L^8H in water, are considered below. In the isostructural $[M(L^7H)_2(L^8H)]^{2+}$ cations, where M = Ni or Zn (Fig. 13), both imino nitroxides L^7H form a five-membered chelate ring with the metal ion, while nitronyl nitroxide L^8H is involved in a six-membered ring. In the reaction with nitroxides containing a heterocyclic moiety in a side chain, the Ni(II) ion cannot initiate redox transformations of the paramagnetic ligand, as it was observed previously in the reactions with paramagnetic Schiff bases $L^1H - L^6H$. Hence, the reaction of Ni(II) salts with nitronyl nitroxide L^8H affords the $[Ni(L^8H)_2(NO_3)_2]$ complex (**26**) containing nitronyl nitroxide as the paramagnetic ligand, while the reaction of Ni(II) with imino nitroxide L^7H gives the $[Ni(L^7H)_2(H_2O)_2](NO_3)_2$ complex (**27**) containing imino nitroxide. Only the reaction of Ni(II) with a mixture of the paramagnetic ligands L^7H and L^8H gives a mixed-radical complex. Complex **24** cannot be synthesized by alternative methods.

This review addresses a new method for the synthesis of heterospin metal complexes with nitroxides mainly in relation to mixed-radical Co(II) and Ni(II) complexes. The Co(II) ion was chosen as a paramagnetic transition metal ion, which can rather readily change the oxidation state, whereas Ni(II), on the contrary, retains the oxidation state under ambient conditions. The use of zinc (**25**) requires a brief comment. The synthesis of metal complexes with stable organic radicals is always followed by an investigation of their structures and magnetic properties. The theoretical analysis of the magnetic properties is a complex issue to address due to numerous exchange channels, which differ

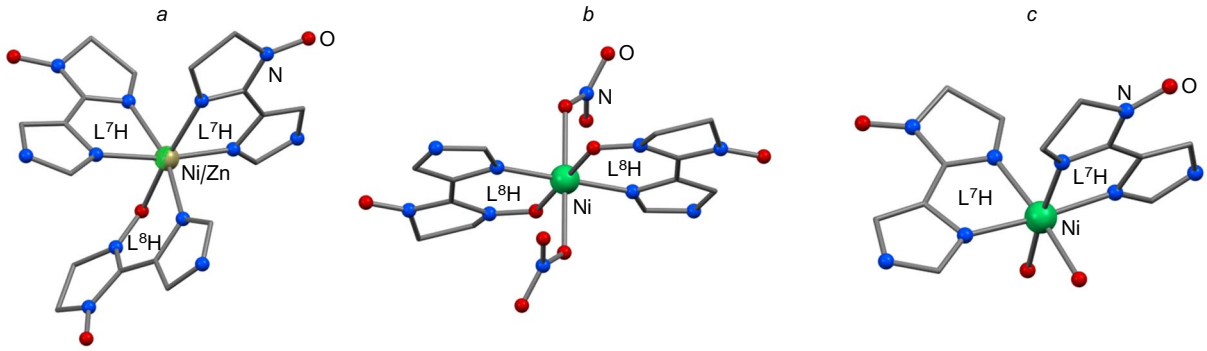


Figure 13. Structures of the $[M(L^7H)_2(L^8H)]^{2+}$ cation, where M = Ni (**24**) or Zn (**25**) (*a*), the $[Ni(L^8H)_2(NO_3)_2]$ molecule (**26**) (*b*) and the $[Ni(L^7H)_2(H_2O)_2]^{2+}$ cation (**27**) (*c*). Compiled from Ovcharenko *et al.*[150]

not only in the value of the exchange integral but also in the sign. Complex **24** is a typical example of such molecules containing numerous intramolecular exchange interaction channels. The problem can be significantly simplified by using, instead of the multispin $[Ni(L^7H)_2(L^8H)]^{2+}$ cation, the isostructural $[Zn(L^7H)_2(L^8H)]^{2+}$ cation (see Fig. 13), in which paramagnetic Ni(II) is replaced by diamagnetic Zn(II).[150]

5. Conclusion

Most of the compounds considered in this review are representatives of a new type of heterospin complexes, which have not been previously known. The goal was to demonstrate that the method for the synthesis of multispin compounds based on the simultaneous introduction of nitronyl nitroxide and imino nitroxide in the reaction with metal provides additional possibilities for the synthesis of heterospin coordination compounds of transition metals with nitroxides. This method has a great synthetic potential. This can be confirmed by the fact that the developed method, the main aspects of which are addressed in the discussion of **1**–**27**, was also applied to prepare related compounds — $[Ni_4(hfa)_2(OH)_2(L^1)_2(L^3)_2(H_2O)_2]\cdot 3\,Me_2CO$ (**28**), $[Co_3(Piv)_2(L^6)_2(L^9)_2]\cdot 2Me_2CO$ (**29**), $[Co_4(hfa)_2(OH)_2(L^1)_2(L^3)_2(H_2O)_2]\cdot 4\,Me_2CO$ (**30**), $[Co_3(Piv)_2(L^3)_2(L^9)_2]\cdot MePh$ (**31**), $K[Mn(L^1)_2(L^2H)]$ (**32**), $[Ni_2(Piv)(L^1)_2(L^{11})(PivH)]$ (**33**), $[Co_3(Piv)_2(L^4)_2(L^5H)_2]$ (**34**), $[Fe(L^1)(L^3)_2]\cdot Me_2CO$ (**35**), $[Fe(L^9)_2(L^{10}H)]$ (**36**) and $[Co_3(Piv)_3(OH)(L^1)(L^4)(PivH)_2]$ (**37**). These compounds are characterized by a different combination of diamagnetic and paramagnetic ligands, or a different composition, or a different nuclearity. It is worth noting that many of the considered compounds can be prepared as various solvates depending on the crystallization conditions. For example, **1** was isolated as the following crystal solvates: $\mathbf{1}\cdot Me_2CO\cdot C_7H_{16}$, $\mathbf{1}\cdot 1.5\,Me_2CO$, $\mathbf{1}\cdot 3\,Me_2CO\cdot C_7H_{16}$, $\mathbf{1}\cdot C_7H_{16}$, $\mathbf{1}\cdot 3\,CH_2Cl_2$, $\mathbf{1}\cdot MeCN\cdot H_2O$ and $\mathbf{1}\cdot MeCN$. This fact should also be taken into account because it is well known that the incorporated solvent molecules can significantly affect the magnetic properties of the compounds.[52, 154–156] Compounds **12**, **19**, **20**, **22**, **24**, **25**, **28** and **33** are of particular interest. They cannot be synthesized by alternative methods. It should be emphasized that the proposed approach allows one to perform reactions of metals with nitronyl nitroxides and imino nitroxides containing different sets of substituents in the paramagnetic organic molecule. Therefore, this method can be used to synthesize an almost unlimited range of multispin compounds.

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