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A New Method for the Synthesis of Heterospin Complexes

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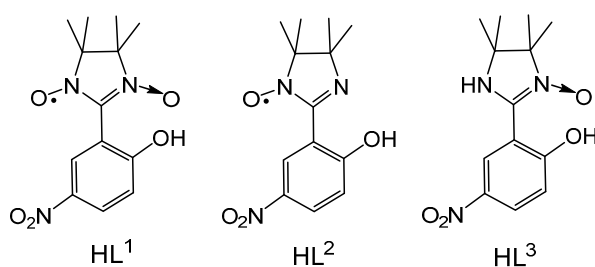* Author to whom correspondence should be addressed; E-Mail: Victor.Ovcharenko@tomo.nsc.ru; Tel.: +7-383-333-1945.

Abstract: The interaction of binuclear Co(II) pivalate $[Co_2(H_2O)Piv_4(HPiv)_4]$ with nitronyl nitroxide HL^1 (2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl) in organic solvents led to the formation of a pentanuclear heterospin complex $[Co_5(Piv)_4L^1_4L^2_2]$. A nontrivial peculiarity of the complex is the presence of both the starting nitronyl nitroxide L^1 and its deoxygenated derivative imino nitroxide L^2 (HL^2: 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl) in its coordination sphere. Based on this, a new synthetic approach was developed, which suggests the use of both the starting radical and the product of its reduction in the reaction with the metal. The suggested approach is a new method for the synthesis of heterospin compounds, including those that cannot be obtained by other methods. It was shown that the reaction of Co(II) pivalate with a mixture of HL^1 and HL^2 can give a trinuclear heterospin complex $[Co_3(Piv)_2L^1_2L^2_2]$. The replacement of Co(II) by Ni(II) completely suppresses the reduction of HL^1 into HL^2, and Ni(II) pivalate does not react with HL^1. The use of a known mixture of HL^1 and HL^2 in the reaction with $[Ni_2(H_2O)Piv_4(HPiv)_4]$, however, led to the formation of a heterospin complex $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$ also containing both nitronyl nitroxide and imino nitroxide.

Keywords: cobalt(II); nickel(II); nitronyl nitroxide; imino nitroxide; redox transformation; new synthetic approach

1. Introduction

Nitroxides have found wide use when solving fundamental problems [1,2]. They are used in radical-mediated polymerization [3,4], for creating rechargeable organic batteries [5,6], as contrast agents for magnetic resonance imaging [7–9] and as organic paramagnets in the synthesis of heterospin molecular magnets [10–16]. Transition metal complexes with nitroxides were used to create heterospin breathing crystals [17]. Nitroxides are widely used in biology, biochemistry and medicine [18–20]. Their behavior in reactions with organic C-centered radicals was actively studied [21]. They are also widely used in the synthesis of various organic derivatives in polymer chemistry [22].

Recently, an unusual process called a "redox-induced change in the ligand coordination mode" was recorded. While reacting with a transition metal, imino nitroxide HL^2 (Scheme 1) showed multifunctional behavior, namely, while reacting with cobalt pivalate, some 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl (HL^2) molecules were reduced to the corresponding nitrone HL^3 (2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide), and an unusual solid product $[Co_3(Piv)_2L^2_2L^3_2]$ containing both the starting imino nitroxide and its reduced diamagnetic analog was isolated. The redox process led to a change not only in the electronic state of the ligand, but also in its coordination mode [23]. The very fact of the formation of $[Co_3(Piv)_2L^2_2L^3_2]$ indicates that there exists an individual class of metal compounds with nitroxides whose ligand shell contains both the starting radical and the product of its reduction.
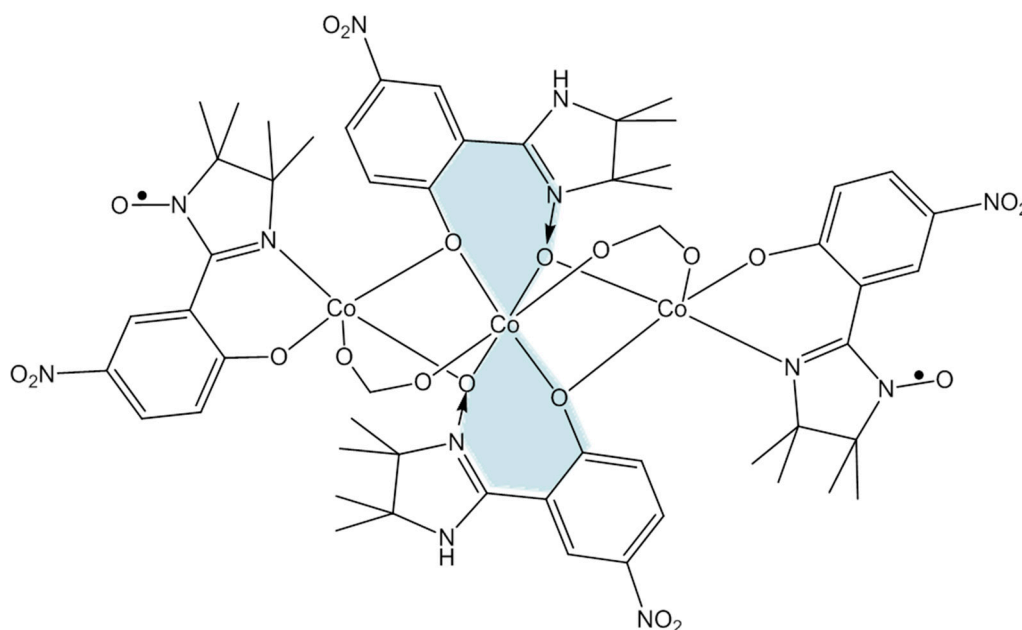

Scheme 1. Nitronyl nitroxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (HL^1), imino nitroxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl (HL^2) and amidine oxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide (HL^3) molecules.

The present paper describes the pentanuclear multispin complex $[Co_5(Piv)_4L^1_4L^2_2]$ formed in the reaction of Co(II) pivalate with nitronyl nitroxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (HL^1). The composition of the complex indicates that some part of HL^1 is reduced to HL^2 during the reaction, because the isolated product contains two radicals: the starting nitronyl nitroxide and its reduced derivative, the corresponding imino nitroxide. In contrast to Co(II) pivalate, Ni(II) pivalate does not react with HL^1 under similar conditions and does not convert it into HL^2, but the reaction of Ni(II) pivalate with a mixture of HL^1 and HL^2 leads to the formation of a heterospin complex $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$ also containing coordinated anions of both nitroxides. Based on the obtained data, a new approach to the synthesis of heterospin compounds is suggested: the reaction of both nitronyl nitroxide and imino nitroxide with the metal. This allowed purposeful synthesis of the $[Co_3(Piv)_2L^1_2L^2_2]$ trinuclear complex containing two different radicals in the coordination shell.
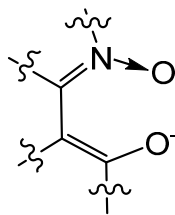
2. Results and Discussion

The synthesis of trinuclear $[Co_3(Piv)_2L^2_2L^3_2]$, where L^2 is the imino nitroxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl anion and L^3 is the corresponding amidine oxide anion (Scheme 1), was described in [23]. The isolation of this compound was a nontrivial problem, because $[Co_3(Piv)_2L^2_2L^3_2]$ crystallized from the reaction mixture only when the starting reagents were used in a strictly definite ratio. In addition, other compounds crystallized along with the desired product, from which they were sometimes separated mechanically. A good yield of $[Co_3(Piv)_2L^2_2L^3_2]$ in the individual state was obtained only when Co(II) pivalate and an equimolar mixture of HL^2 and HL^3 were used as reagents. This should be taken into account, because below, we make a certain analogy between the reaction of Co(II) pivalate with a mixture of HL^2 and HL^3 and the reaction of Co(II) pivalate with a mixture of HL^1 and HL^2.

In the heterospin $[Co_3(Piv)_2L^2_2L^3_2]$ molecule, both L^2's perform the function of terminal chelate ligands, which form six-membered metallocycles typical for Schiff bases. The L^3 anions are coordinated as bridging tetradentate ligands; the "central" cobalt atom forms seven-membered metallocycles with them (Scheme 2).
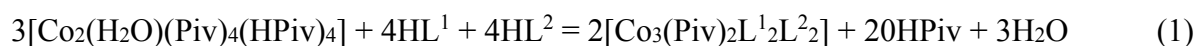

Scheme 2. Seven-membered metallocycles formed by L^3 with the "central" cobalt atoms in the trinuclear $[Co_3(Piv)_2L^2_2L^3_2]$ molecule.

We noticed that the L^3 donor group that formed seven-membered metallocycles in the $[Co_3(Piv)_2L^2_2L^3_2]$ molecule (Scheme 2) was identical to that in nitronyl nitroxide HL^1. This prompted us to study the product of the interaction of Co(II) pivalate with the equimolar mixture of HL^1 and HL^2. The isostructural character of the L^1 and L^3 donor group (Scheme 3) was assumed to be favorable for purposeful introduction of L^1 in the complex molecule to ultimately obtain a multispin complex containing two different paramagnetic ligands.
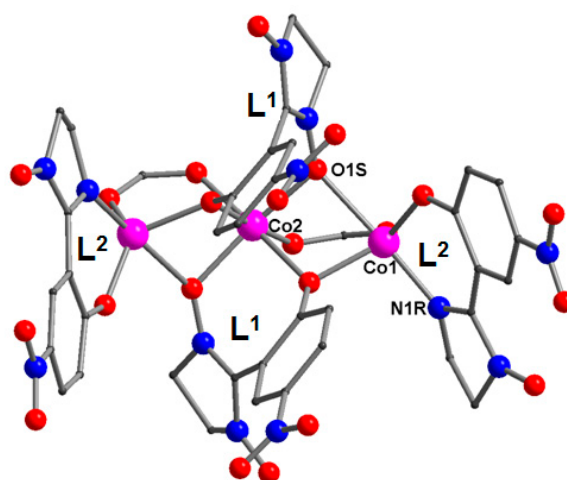
Scheme 3. The L^1 and L^3 donor group, which is favorable for the formation of seven-membered metallocycles.

Indeed, the reaction of binuclear Co(II) pivalate with a mixture of nitroxides HL^1 and HL^2 gave a trinuclear $[Co_3(Piv)_2L^1_2L^2_2]$ complex, which contained both nitroxides. The maximum yield of the product (70%) was obtained at a molar ratio of reagents $[Co_2(H_2O)(Piv)_4(HPiv)_4]:HL^1:HL^2 = 3:4:4$, corresponding to the stoichiometric coefficients of the reaction:

$$3[Co_2(H_2O)(Piv)_4(HPiv)_4] + 4HL^1 + 4HL^2 = 2[Co_3(Piv)_2L^1_2L^2_2] + 20HPiv + 3H_2O \qquad (1)$$

The trinuclear molecule of the complex (Figure 1), which crystallized as a solvate with two acetone molecules $[Co_3(Piv)_2L^1_2L^2_2]\cdot2Me_2CO$, is isostructural with $[Co_3(Piv)_2L^2_2L^3_2]$. The "terminal" cobalt atoms form six-membered metallocycles with the coordinated imino nitroxides. The "central" Co atom forms seven-membered metallocycles with nitronyl nitroxides, which perform the cyclic bridging tetradentate function. The trigonal-bipyramidal environment of the terminal cobalt atoms is formed by the N atom of the nitroxyl fragment (Co_1-N1R 2.024(3) Å), two O_{Ph} atoms of the phenoxy groups L^2 and L^1, the O_{Piv} atom and the bridging O_{NO} atom of the nitroxyl group L^1 at distances of 1.907(2)–2.311(3) Å. The octahedral environment of Co_2 (the symmetry of the environment is C_2) is formed by two O_{Piv} (2.042(2) Å), two μ-O_{NO} (2.033(2) Å) and two μ-O_{Ph} (2.108(2) Å) atoms.

Thus, the interaction of Co(II) pivalate with an equimolar mixture of nitronyl and imino nitroxides is an effective method for the synthesis of the heterospin $[Co_3(Piv)_2L^1_2L^2_2]$ complex containing two different paramagnetic ligands.
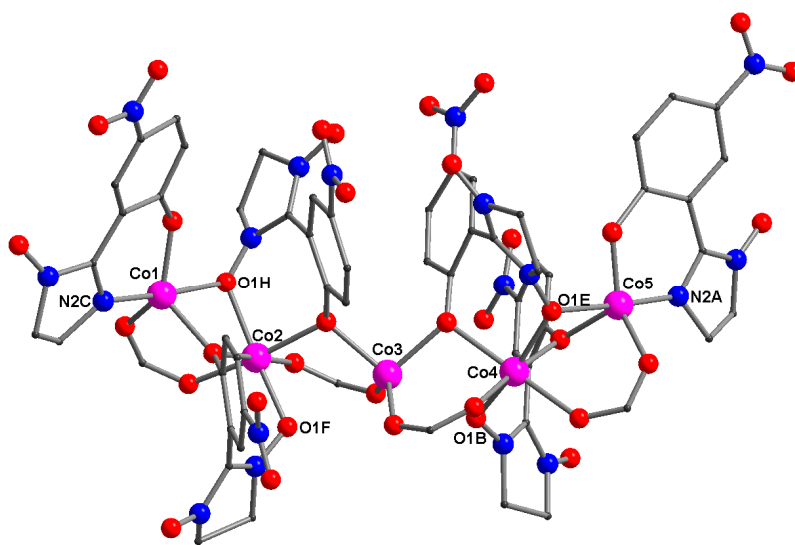

Figure 1. Trinuclear $[Co_3(Piv)_2L^1_2L^2_2]$ molecule. Hereinafter, small black balls, C; magenta, Co; red, O; blue, N; the H atoms and the CH_3 and Bu^t groups are omitted.

If imino nitroxide is not introduced in the reaction mixture and only nitronyl nitroxide HL^1 is used in the reaction with Co(II) pivalate, the solid product is the pentanuclear heterospin compound $[Co_5(Piv)_4L^1_4L^2_2]\cdot 0.5Me_2CO\cdot 0.5C_7H_{16}$. It also contains nitroxides L^1 and L^2 in the ligand shell. In this case, L^2 forms as a consequence of the redox process, in which L^1 is deoxygenated. The complex forms by the reaction of cobalt pivalate with HL^1 in an acetone/heptane mixture with an initial ratio of reagents $[Co_2(H_2O)Piv_4(HPiv)_4]:HL^1$ from 1:1–1:4; the product yield can reach 50%–60%. The maximum yield of $[Co_5(Piv)_4L^1_4L^2_2]\cdot 0.5Me_2CO\cdot 0.5C_7H_{16}$ (70%) was achieved in an alternative synthesis in one of the experiments at an initial molar ratio of reagents of $[Co_2(H_2O)(Piv)_4(HPiv)_4]:HL^1:HL^2 = 5:8:4$, corresponding to the stoichiometric coefficients of the reaction:

$$5[Co_2(H_2O)Piv_4(HPiv)_4] + 8HL^1 + 4HL^2 = 2[Co_5(Piv)_4L^1_4L^2_2] + 32HPiv + 5H_2O \qquad (2)$$

Note, however, that the use of the known mixture of HL^1 and HL^2 with the indicated reagent ratio in the synthesis often leads to crystallization of a mixture of $[Co_5(Piv)_4L^1_4L^2_2]\cdot 0.5Me_2CO\cdot 0.5C_7H_{16}$ and $[Co_3(Piv)_2L^1_2L^2_2]\cdot 2Me_2CO$ that can hardly be separated.

The pentanuclear molecule has three different environments of Co atoms: tetrahedral for the "central" Co_3, octahedral for the "internal" Co_2 and Co_4 and trigonal bipyramidal for the "terminal" Co_1 and Co_5 (Figure 2).

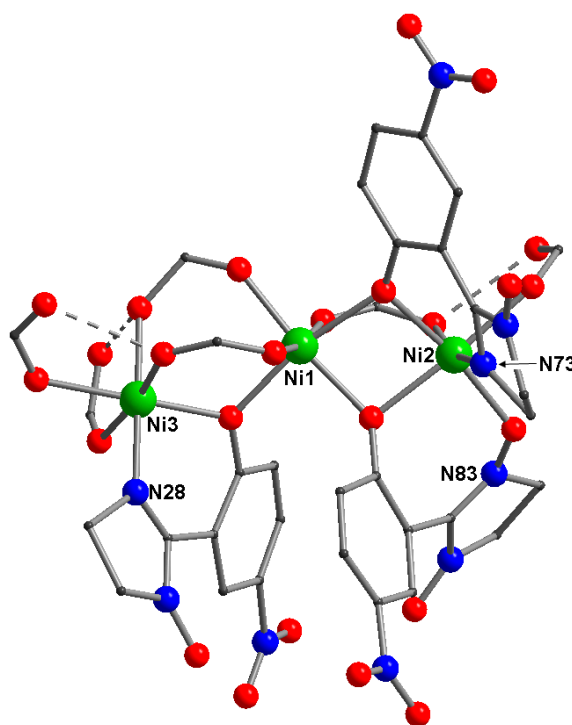**Figure 2.** Structure of the pentanuclear $[Co_5(Piv)_4L^1_4L^2]$ molecule.

The $[Co_5(Piv)_4L^1_4L^2_2]$ molecule contains fragments similar to those of $[Co_3(Piv)_2L^1_2L^2_2]$; namely, the environment of the Co_1 and Co_5 atoms in Figure 2 is the same as that of Co_1 in Figure 1; the environment of Co_2 and Co_4 in Figure 2 is the same as that of Co_2 in Figure 1. In $[Co_5(Piv)_4L^1_4L^2_2]$ molecules, as well as in $[Co_3(Piv)_2L^1_2L^2_2]$ molecules, the "terminal" cobalt atoms (Co_1 and Co_5) form six-membered metallocycles typical for Schiff bases with the coordinated imino nitroxides, and the Co_2 and Co_4 atoms form seven-membered metallocycles with nitronyl nitroxides. All of the O_{Ph} atoms of the phenoxy groups L^1 perform the bridging function. Half of all nitroxyl O_{NO} atoms (O1E and O1H) are also involved in the formation of bridging bonds, while the other half (O1B and O1F) are coordinated as monodentate ligands by the Co_2 and Co_4 atoms, respectively. The Co–N bond lengths are 2.039(5) and 2.041(7) Å;

the Co–O bond lengths are 1.909(5)–2.269(5) Å. The Co–O1B and Co–O1F distances are long enough, 2.580(4) and 2.836(5) Å; as a result, the "central" Co_3 atom has a tetrahedral environment.

Earlier, it was reported [23] that when HL^2 reacted with nickel pivalate $[Ni_2(H_2O)(Piv)_4(HPiv)_4]$, imino nitroxide did not undergo any transformations. When Ni(II) pivalate reacted with HL^1, nitronyl nitroxide also did not undergo any redox transformations. Moreover, no products of interaction of Ni(II) pivalate with L^1 were isolated irrespective of the starting reagent ratio and synthesis conditions (when the solution was concentrated, the solid product was primarily unchanged HL^1). The introduction of both HL^1 and HL^2 in the reaction system, however, led to the formation of a mixed-ligand complex $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$, as in the case of cobalt. The highest yield of the complex (60%) can be achieved when using the molar ratio of reagents $[Ni_2(H_2O)(Piv)_4(HPiv)_4]:HL^1:HL^2 = 3:2:4$ corresponding to the stoichiometric coefficients of the reaction:

$$3[Ni_2(H_2O)(Piv)_4(HPiv)_4] + 2HL^1 + 4HL^2 = 2[Ni_3L^1L^2_2(Piv)_3(HPiv)_3] + 12HPiv + 3H_2O \qquad (3)$$

The structure and composition of $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$ differ from those for the trinuclear Co(II) complex with L^1 and L^2 (*cf.* Figures 1 and 3). All of the Ni atoms have an octahedral environment. The paramagnetic ligands perform the bridging cyclic tridentate function. Each monodentate coordinated HPiv molecule forms an H-bond with one of the O atoms of the neighboring μ_2–O,O'-pivalate anion. The Ni–N distances are 2.062(4) and 2.106(3) Å; the Ni–O distances are 1.977(3) and 2.121(4) Å.

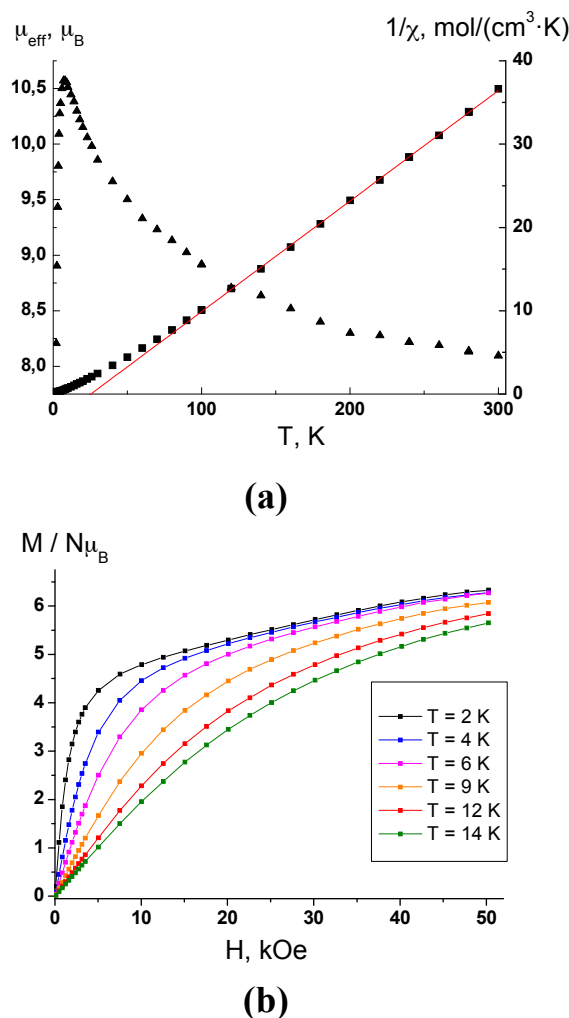**Figure 3.** Molecular structure of $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$.

Thus, the factors that favor the synthesis of $[Co_5(Piv)_4L^1_4L^2_2]$ by the reaction of Co(II) pivalate with L^1 are the ability of the metal to be at different oxidation levels and the kinetic stability of both the starting L^1 and the formed L^2. When Ni(II) pivalate was used in the reaction with L^1, the complexes containing L^2 were never recorded. This is fully consistent with the data of [23–27], where the authors also used the metals capable of changing the oxidation level.

Regarding the redox processes with nitroxides, it was noted that in the reaction with a transition metal, the nitroxide can be reduced to the corresponding hydroxylamine [28,29] and form the product of cocrystallization of the starting radical and the complex with nitrone [30] or complex with coordinated hydroxylamine [31]. Co(hfac)$_2$ is able to reduce the ferrocenyl bis(nitronyl nitroxide) with producing the diamagnetic ferrocenyl bis(amidine oxide) cation, which forms with the [Co(hfac)$_3$]$^-$, as the counterion, the complex salt [32]. Several products are known in which hydroxylamine reduced the metal and was itself oxidized to the corresponding nitroxide [33]. When the products of the interactions of metals with dinitroxides were studied, unusual compounds were isolated, in which one of the nitroxyl groups was reduced to the hydroxylamine anion during the reaction [24,25,34]. The oxidation of the transition metal induced by the reduction of one of the coordinated nitroxides was described in [26,27]. A specific copper(II)–nitroxide complex was described, which has a nontrivial structural peculiarity: it contains both the coordinated O atoms of nitroxide and those of the corresponding hydroxylamine anion [35]. An interesting manganese(II)–nitroxide–hydroxylamine complex was known, as well [36]. In the case of the interaction of transition metal compounds with L^2 [23] and of Co(II) pivalate with L^1, we found that heterospin complexes could be obtained, which contained both the starting nitroxide and the product of its reduction as a result of the transition metal-catalyzed transformation of the starting radical.

The pathway of the ligand reduction has not been established, but it is probably not a simple process [28,31,32,34]. However, the redox process can be suppressed in the synthesis of heterospin compounds of transition metals containing both nitronyl nitroxide and imino nitroxide or imino nitroxide and the corresponding nitrone (or hydroxylamine). Since nitronyl nitroxide, imino nitroxide and the corresponding nitrone are often kinetically stable and can be isolated in the individual state, a known mixture of components can be used in the synthesis, as was done in the case of the synthesis of [Co$_3$(Piv)$_2$L$^1_2$L$^2_2$] and [Ni$_3$L^{1}L$^2_2$(Piv)$_3$(HPiv)$_3$]. This is especially important in the latter case. Since Ni(II) does not initiate the transformation of L^1 into L^2, [Ni$_3$L^{1}L$^2_2$(Piv)$_3$(HPiv)$_3$] cannot be synthesized by any other procedure. Therefore, this is actually a new method for the synthesis of heterospin complexes: the reaction of a metal compound with a mixture of nitronyl nitroxide and imino nitroxide or with a mixture of imino nitroxide and the corresponding nitrone.

The multispin molecules of the multinuclear complexes in question have a rather complex system of exchange channels, which requires a separate detailed study in each case. Since this study concentrated on the new approach to the synthesis of heterospin complexes, the magnetic properties of the isolated products are presented below in concise fractographic form.
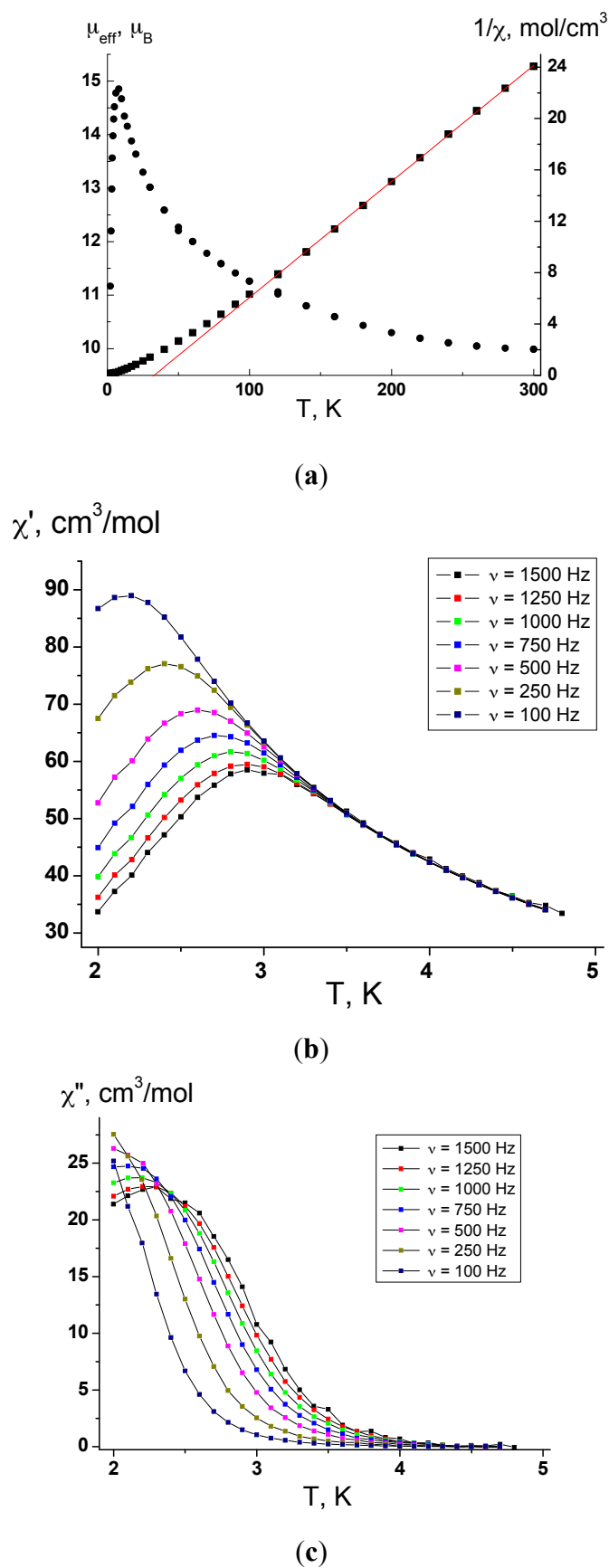
For [Co$_3$(Piv)$_2$L$^1_2$L$^2_2$]·2Me$_2$CO, μ_{eff}, which is 8.09 μ_B at 300 K, gradually increased to 10.57 μ_B when the temperature decreased to 8 K (Figure 4a). In the temperature range 100–300 K, the dependence $1/\chi(T)$ obeys the Curie–Weiss law. The optimum values of the Curie (C) and Weiss (θ) constants are 7.54 ± 0.03 cm^3·K/mol and 25.4 ± 0.8 K, respectively. The positive value of the Weiss constant θ suggests that the ferromagnetic exchange interactions are dominant. For [Co$_3$(Piv)$_2$L$^1_2$L$^2_2$]·2Me$_2$CO, the dependence of magnetization on the strength of the external magnetic field below 14 K is nonlinear and cannot be described in terms of the Brillouin function (Figure 4b). This points to the transition of the substance into the magnetically-ordered state with spontaneous magnetization 26,000 cm^3·G/mol at 2 K. The Curie temperature T$_C$ can be estimated at 5 K.

Figure 4. Temperature dependences of μ_{eff} and $1/\chi$ (**a**) and M(H) at different temperatures (**b**) for $[Co_3(Piv)_2L^1_2L^2_2]\cdot2Me_2CO$.

For $[Co_5(Piv)_4L^1_2L^2_4]\cdot0.5Me_2CO\cdot0.5C_7H_{16}$, μ_{eff} is 9.99 μ_B at 300 K and gradually increased to 14.85 μ_B when the temperature decreased to 8 K; then, it decreased abruptly to 11.17 μ_B at 2 K. Note that the high-temperature value of μ_{eff} is considerably higher than the theoretical pure spin value of 7.55 μ_B for nine non-interacting paramagnetic centers (three Co(II) ions (S = 3/2, g = 2) and four nitroxides (S = 1/2, g = 2)) due to the orbital contribution that is typical for Co(II) ions in an octahedral environment. In the temperature range 100–300 K, the dependence $1/\chi(T)$ obeys the Curie–Weiss law. The optimum values of the Curie (C) and Weiss (θ) constants are 11.07 $\pm$ 0.04 cm$^3\cdot$K/mol and 32.8 $\pm$ 0.6 K, respectively. For $[Co_5(Piv)_4L^1_2L^2_4]\cdot0.5Me_2CO\cdot0.5C_7H_{16}$, the dependence of magnetization on the strength of the external magnetic field below 10 K is nonlinear. A study of the magnetic susceptibility of $[Co_5(Piv)_4L^1_2L^2_4]\cdot0.5Me_2CO\cdot0.5C_7H_{16}$ in an alternating magnetic field (Figure 5) showed that the temperature dependence of the out-of-phase component of magnetic-susceptibility $\chi''(T)$ has a maximum, which shifts toward low temperatures when the frequency of the alternating magnetic field decreases. The appearance of the out-of-phase component $\chi''(T)$ is one of the characteristics of single-molecule magnets (SMM). The maximum of χ'' was not observed for all frequencies; the rough estimation of the energy barrier (E_a) based on the Arrhenius equation $\ln(2\pi\nu) = \ln(1/\tau_0) + E_a/(k_BT)$ gave $E_a/k_B = 3.1$ K.

(**a**)

(**b**)

(**c**)

Figure 5. Temperature dependences of μ_{eff} and $1/\chi$ (**a**) and plot of the in-phase χ' (**b**) and out-of-phase χ'' (**c**) components of AC susceptibility at different frequencies (ν) as a function of temperature for $[Co_5(Piv)_4L^1_2L^2_4]\cdot0.5Me_2CO\cdot0.5C_7H_{16}$.

The dependence $\mu_{eff}(T)$ for $[Ni_3L^1_2L^2(Piv)_3(HPiv)_3]$ is presented in Figure 6. The μ_{eff} value at 300 K is 6.01 μ_B and does not change when the temperature decreases to 100 K. Below 100 K, μ_{eff} gradually increases, reaching 6.32 μ_B at 10 K, and then abruptly decreases to 5.28 μ_B at 2 K. In the temperature range 10–300 K, the dependence $1/\chi(T)$ obeys the Curie–Weiss law. The optimum values of the Curie (C) and Weiss (θ) constants are 4.45 ± 0.01 cm^3·K/mol and 2.4 ± 0.2 K, respectively. The high-temperature value of μ_{eff} agrees well with the theoretical pure spin value 5.74 μ_B for six non-interacting paramagnetic centers (three Ni(II) ions with spin S = 1 and three nitroxides with spins S = 1/2 at a g factor of two. The increased μ_{eff} at lower temperatures and the positive Weiss constant θ indicate that weak ferromagnetic exchange interactions between the spins of the paramagnetic centers dominate.

Figure 6. Temperature dependences of μ_{eff} and $1/\chi$ for $[Ni_3L^1_2L^2(Piv)_3(HPiv)_3]$.

3. Experimental Section

The binuclear pivalates $[Co_2(H_2O)(Piv)_4(HPiv)_4]$ and $[Ni_2(H_2O)(Piv)_4(HPiv)_4]$ were prepared as described in [37]. The synthesis of HL^1 and HL^2 was described in [38].

3.1. Synthesis of $[Co_3(Piv)_2L^1_2L^2_2]\cdot 2Me_2CO$

A solution of a mixture of HL^1 (0.021 g, 0.07 mmol) and HL^2 (0.02 g, 0.07 mmol) in acetone (3 mL) was added to the solution of $[Co_2(H_2O)(Piv)_4(HPiv)_4]$ (0.05 g, 0.053 mmol) in acetone (2 mL) at room temperature. Then, heptane (3 mL) was added to the reaction mixture, and the mixture was stirred until it became transparent. The reaction mixture was kept in an open flask for 2 days. Its volume decreased, and brown prismatic crystals precipitated, which were filtered off, washed with a cooled mixture of acetone and heptane (1:3) and dried with an air current. Yield 70%. Anal. calcd. for $C_{68}H_{90}N_{12}Co_3O_{24}$ (%): C, 49.9; H, 5.5; N, 10.3. Found (%): C, 49.8; H, 5.4; N, 10.0.

3.2. Synthesis of [Co$_5$(Piv)$_4$L$^1_4$L$^2_2$]·0.5Me$_2$CO·0.5C$_7$H$_{16}$

A solution of HL^1 (0.025 g, 0.084 mmol) in acetone (2 mL) was added to the solution of [Co$_2$(H$_2$O)(Piv)$_4$(HPiv)$_4$] (0.04 g, 0.042 mmol) in acetone (3 mL) at room temperature. Then, heptane (3 mL) was added, and the mixture was stirred until the solution became transparent. After the solution was kept for 2 or 3 days, brown elongated crystals precipitated. They were filtered off, washed with cold acetone and dried with an air current. Yield 50%–60%. Anal. calcd. for C$_{206}$H$_{274}$N$_{36}$Co$_{10}$O$_{73}$ (%): C, 49.4; H, 5.5; N, 10.1. Found (%): C, 49.7; H, 5.6; N, 9.5.

[Co$_5$(Piv)$_4$L$^1_4$L$^2_2$]·0.5Me$_2$CO·0.5C$_7$H$_{16}$ also formed at an initial reagent ratio of [Co$_2$(H$_2$O)(Piv)$_4$(HPiv)$_4$]:HL^1 = 1:1 or 1:4. In the former case, however, the crystals of the complex were contaminated with an unidentified blue gel-like product; in the latter case, with the crystals of excess nitroxide HL^1. The highest yield of [Co$_5$(Piv)$_4$L$^1_4$L$^2_2$]·0.5Me$_2$CO·0.5C$_7$H$_{16}$ (70%) was obtained when binuclear Co(II) pivalate, HL^1 and HL^2 were used as the starting reagents in a ratio of 5:8:4, which corresponds to the stoichiometric coefficients of the reaction:

$$5[Co_2(H_2O)Piv_4(HPiv)_4] + 8HL^1 + 4HL^2 = 2[Co_5(Piv)_4L^1_4L^2_2] + 32HPiv + 5H_2O \qquad (4)$$

3.3. Synthesis of [Ni$_3$L^{1}L$^2_2$(Piv)$_3$(HPiv)$_3$]

A mixture of [Ni$_2$(H$_2$O)(Piv)$_4$(HPiv)$_4$] (0.05 g, 0.053 mmol), HL^1 (0.01 g, 0.034 mmol) and HL^2 (0.019 g, 0.068 mmol) was dissolved in acetone (3 mL) in a dry N$_2$ atmosphere at room temperature (MBraun chamber). Then, heptane (5 mL) was added to the resulting dark red solution. The reaction mixture was kept in an open flask for 3 or 4 days, after which dark claret red crystals were filtered off. Yield 77%. Anal. calcd. for C$_{69}$H$_{102}$Ni$_3$N$_9$O$_{25}$ (%): C, 50.7; H, 6.3; N, 7.7. Found (%): C, 51.2; H, 6.5; N, 7.6.

3.4. Crystal Structure Determination

The X-ray diffraction (XRD) experiments were performed on a SMART APEX II CCD and APEX DUO (Bruker AXS) diffractometer (Mo Kα for Co complexes and Cu Kα for the Ni complex). All of the structures were solved by direct methods and refined by full-matrix least-squares analysis in an anisotropic approximation for non-hydrogen atoms. The positions of the majority of H atoms were calculated. The methyl H atoms were refined isotropically in a rigid group approximation. Hydrogen atoms were refined isotropically with the use of geometrical constraints. Since the solvent molecules in {Co$_5$} and {Ni$_3$} complexes could not be modeled properly, they were squeezed out with PLATON [27,39]. All calculations were performed with the Bruker SHELXTL (Version 6.14) and SHELXL (Version 2014/6) program packages [40]. The crystal data and details of experiments are given in Table 1. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

Table 1. Crystal data and the details of the experiments for the complexes.

Compound	$[Co_3(Piv)_2L^1_2L^2_2]\cdot 2Me_2CO$	$[Co_5(Piv)_4L^1_4L^2_2]$	$[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$
FW	1636.30	2426.82	1633.73
T, K	240	296	240
Space group, Z	$C2/c$, 4	$P2_1/c$, 4	$P2_1/c$, 4
a, Å	20.3249(15)	21.7158(6)	25.791(3)
b, Å	17.0770(14)	21.4802(6)	16.4283(18)
c, Å	23.602(3)	28.1954(7)	23.722(2)
β, °	106.553(6)	103.044(2)	116.538(5)
V, Å^3	7852.3(12)	12812.6(6)	8991.9(17)
D_c, g·cm^{-3}	1.384	1.258	1.207
θ_{max}, °	28.008	28.331	67.628
I_{hkl} (meas/uniq)	33,218/9349	117,351/31,674	67,564/15,783
R_{int}	0.1338	0.1363	0.1176
I_{hkl} (obs)	3110	8829	6251
Parameters	520	1507	956
GooF	0.751	0.898	0.851
R_1/wR_2 ($I > 2\sigma_I$)	0.0462/0.757	0.0777/0.1948	0.0663/0.1669
R_1/wR_2 (all data)	0.1875/0.1013	0.27481/0.2871	0.1532/0.2064
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.363, −0.256	0.711, −0.396	0.643, −0.430
CCDC deposition	1419127	1419128	1419126

3.5. Magnetic Measurements

The magnetic susceptibility of the polycrystalline samples was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 2–300 K with a magnetic field of up to 5 kOe. The diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$. The AC magnetic susceptibility was measured in an oscillating AC field of 3.5 G and a zero DC field. The oscillation frequencies were in the range 98–1488 Hz.

4. Conclusions

Thus, our study showed that the reaction of Co(II) pivalate with nitronyl nitroxide HL^1 forms a pentanuclear complex [Co$_5$(Piv)$_4$L$^1_4$L$^2_2$], whose molecule has both the starting nitronyl nitroxide L^1 and its imino nitroxide analog L^2. This prompted us to introduce a known mixture of HL^1 and HL^2 in the reaction. It appeared that this synthetic technique (the use of both the starting radical and the product of its reduction in the reaction with the metal) can serve as an independent method for the synthesis of heterospin complexes. It was shown that the interaction of Co(II) pivalate with nitroxides at a molar ratio of reagents of [Co$_2$(H$_2$O)(Piv)$_4$(HPiv)$_4$]:HL^1:HL^2 = 3:4:4 gives the trinuclear heterospin complex [Co$_3$(Piv)$_2$L$^1_2$L$^2_2$] with a high yield. The replacement of Co(II) by Ni(II) completely suppresses the reduction of HL^1 into HL^2. In addition, Ni(II) pivalate does not react with HL^1. However, the use of the known mixture of HL^1 and HL^2 in the reaction with [Ni$_2$(H$_2$O)Piv$_4$(HPiv)$_4$] is an effective method for the synthesis of the heterospin complex [Ni$_3$L^{1}L$^2_2$(Piv)$_3$(HPiv)$_3$], which also contains both nitronyl and imino nitroxides.

Thus, the results of the present study open up a new opportunity in the synthesis of heterospin complexes. Since both nitronyl and imino nitroxides and the corresponding nitrone (the product of more profound reduction) are generally kinetically-stable products, their binary mixtures can readily be prepared. The use of these mixtures in reactions with transition metals can lead to multispin complexes, including $[Co_3(Piv)_2L^1_2L^2_2]$ and $[Ni_3L^1L^2_2(Piv)_3(HPiv)_3]$, which were obtained only using the known mixture of nitronyl nitroxide and its imino nitroxide derivative as the starting reagent.

Acknowledgments

Author Contributions

Olga Kuznetsova and Elena Fursova performed the experiments on the synthesis of heterospin complexes and the growth of high-quality crystals. Galina Romanenko carried out an X-ray diffraction study of the single crystals of the compounds. Artem Bogomyakov performed magnetochemical measurements. Victor Ovcharenko formulated the idea and wrote the manuscript, which was revised and accepted by all of the co-authors.

Conflicts of Interest

The authors declare no conflict of interest.

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