Polynuclear $Co^{II,III}$ compounds containing pivalate and hexafluoroacetylacetonate anions in the ligand shell and their heterospin complexes with nitroxides

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The reaction of cobalt(II) bis(hexafluoroacetylacetonate) ($Co(hfac)_2$) with polynuclear Co^{II} or $Co^{II,III}$ pivalates, $[Na_2Co_4(OH)_2(Piv)_8(EtOH)_4]$, $[Co_2(H_2O)(Piv)_4(HPiv)_4]$, and $[Co^{III}{}_2Co^{II}{}_4(O)_2(Piv)_{10}(H_2O)(THF)_3]\cdot 1.5THF$ (Piv is pivalate), affords the previously unknown cobalt compounds containing coordinated Piv and hfac anions in the ligand shell, *viz.*, the dinuclear complex $[Na_2Co_2(hfac)_4(Piv)_2(Me_2CO)_4]$, the tetranuclear complex $[Co_4(Piv)_4(hfac)_2(OH)_2(HPiv)_4]\cdot HPiv$, and the tetradecanuclear complex $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2HPiv\cdot 2H_2O\cdot 3C_7H_{16}$, respectively. The tetradecanuclear complex has an unusual ability to precipitate nitroxides from solution, due to which the following new heterospin crystalline solids were synthesized: $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_2(HPiv)_2]\cdot 2NIT\text{-}Me\cdot 2HPiv\cdot C_6H_{14}$, $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2NIT\text{-}Et\cdot 2CHCl_3$, $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2NIT\text{-}Ph\cdot 2C_6H_{14}$, $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2L^1\cdot 2CH_2Cl_2$, and $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2L^2\cdot C_6H_{14}$, where NIT-Me, NIT-Et, and NIT-Ph are 2-imidazoline nitroxides, L^1 is 3-imidazoline nitroxide, and L^2 is di-*tert*-butyl nitroxide. The X-ray diffraction study showed that the efficient binding of nitroxides is provided by the specific arrangement of the μ_3-OH groups in the $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]$ molecule, which is spatially complementary for the formation of numerous hydrogen bonds with the nitroxide moiety. The coordination of the nitroxides by terminal cobalt ions is impossible because this would lead to the impermissible spatial overlap of the atoms of the tetradecanuclear moiety and the nitroxide. The spatial characteristics of only NIT-H containing the H atom in position 2 of the 2-imidazoline ring are suitable for the direct coordination of the nitroxide, which made it possible to synthesize the complex $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_4(NIT\text{-}H)_2]\cdot 4HPiv\cdot 2H_2O$.

Key words: cobalt, polynuclear compounds, pivalates, hexafluoroacetylacetonates, nitroxides, X-ray diffraction analysis, magnetic susceptibility.

The reactions of polynuclear metal compounds with nitroxides provide an efficient route to multispin compounds.[1—11] The resulting complexes are called heterospin complexes because they contain paramagnetic centers simultaneously with unpaired d (or f) and p electrons. These centers differ in the electron spin, the g factor, and the character of the spatial distribution of the unpaired electron density. Due to the presence of several paramagnetic centers in heterospin molecules, the magnetic properties of these compounds have attracted considerable interest because these compounds are convenient objects for studying fine features of exchange interactions. Among these compounds, there are solid phases exhibiting the bulk magnetization.[1,6,8] However, this synthetic approach is often complicated by the low solubility of the starting polynuclear complexes in organic solvents, due to which they cannot be introduced into the reactions with nitroxides. In addition, metal ions of polynuclear moieties should have strong acceptor properties to coordinate weak donors (O atoms of nitroxide moieties). The acceptor ability of the terminal atoms of polynuclear moieties can be enhanced by introducing ligands with acceptor properties into the coordination environment of the metal atoms. Recently, it has been shown that the reaction of

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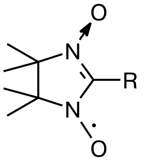
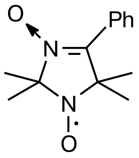
$KNi_4(Piv)_7(OH)_2(EtOH)_6$ with Ni^{II} hexafluoroacetylacetonate in an acetone—heptane mixture affords polynuclear complexes containing both pivalate (Piv) and hexafluoroacetylacetonate (hfac) anions in the ligand shell.[11] In the present study, we investigated the possibility of the use of the similar synthetic approach based on the reaction of $Co(hfac)_2$ with polynuclear cobalt pivalates for the preparation of mixed-ligand cobalt Piv hfac compounds. This approach proved to be efficient and allows the synthesis of this type of mixed-ligand polynuclear compounds, although their compositions and structures substantially differ from those found[11] for Ni^{II} complexes. In the present study, we describe procedures for the synthesis of the previously unknown polynuclear cobalt compounds containing both Piv and hfac ligands and report on the structures and magnetic properties of these compounds. The unusual reaction of the tetradecanuclear complex $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]$ with nitroxides NIT-Me, NIT-Et, NIT-Ph, 3-imidazoline nitroxide (L^1), and di-*tert*-butyl nitroxide (L^2), which contain no functional groups other than $O^{\bullet}$—N<, was investigated. This reaction affords heterospin compounds. In the solid state, nitroxides in these compounds are bound in an unusual way through hydrogen bonds with tetradecanuclear molecules. Only NIT-H molecules have such a structure that allows them to penetrate into the Piv hfac ligand shell and to be coordinated to Co^{II} ions.

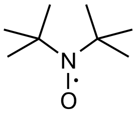


NIT-R

R = H, Me, Et, Ph



L^1



L^2

Results and Discussion

In the study of the reaction products of various cobalt pivalates with $Co(hfac)_2$ under ambient conditions, we isolated di-, tetra-, and tetradecanuclear complexes containing both Piv and hfac anions in the ligand shell from mixtures of acetone and heptane. The nuclearity of the reaction products is determined by the nature of the starting cobalt pivalate.

In first experiments, the complex $[Na_2Co_4(OH)_2(Piv)_8(EtOH)_4]$ (**1**), which is readily soluble in organic solvents, was used as the starting pivalate. This complex was synthesized by the reaction of $CoCl_2$ with a fivefold excess of NaPiv in EtOH. The structure of **1** can be described as a derivative of the known[12] tetranuclear complex $[Co_4(OH)_2(Piv)_6(EtOH)_6]$, in which two EtOH molecules are replaced by moieties consisting of Na ditetrahedra (Fig. 1). The distorted tetrahedral environment of the Na atoms is formed by O atoms of the bridging Piv ligands (Na—O, 2.205(6)—2.350(6) Å). The coordination environment of the Co atoms can be described as distorted octahedra (the Co—O distances are in the range of 1.991(5)—2.198(6) Å) (Table 1).

The reaction of **1** with $Co(hfac)_2$ in an acetone—heptane mixture afforded the complex $[Na_2Co_2(hfac)_4(Piv)_2(Me_2CO)_4]$ (**2**) (Fig. 2). The octahedral environment of the Co atoms in ionic associate **2** is formed by four O atoms of two hfac ligands (d_{Co-O} = 2.063(4)—2.073(3) Å) and two O atoms of the bridging Piv ligands (d_{Co-O} = 2.063(3) Å, d_{Co-O} = 2.065(3) Å). The coordination environment of each Na atom is also formed by six O atoms belonging to two hfac ligands, two Piv ligands, and two acetone molecules, as is shown in Fig. 2 (d_{Na-O} = 2.293(7)—2.541(3) Å).

Associate **2** can also be synthesized by the reaction of equimolar amounts of $Co(hfac)_2$ and NaPiv in an acetone—heptane mixture; however, in this case the isolation of crystals of the target compound presents difficulties because they form intergrowths with crystals of the starting bis-chelate that precipitate simultaneously. It should be noted that crystals of complex **2** are rapidly decomposed in air due to the loss of acetone molecules. As is mentioned in the Experimental section, the use of KPiv instead of NaPiv leads to the formation of the complex $[K_2Co_2(hfac)_4(Piv)_2(Me_2CO)_4]$ (**2a**) isostructural with **2**.

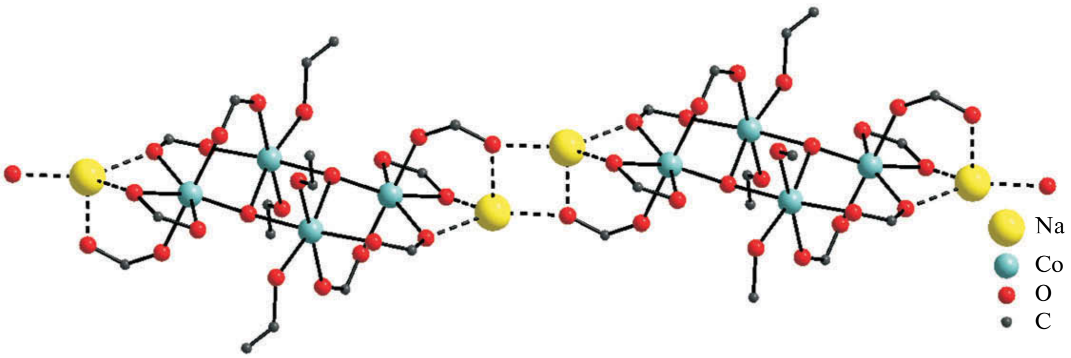


Fig. 1. Structure of the chain in **1**. The H atoms and the Bu^t groups are not shown.*

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* Figures 1—7 are available in full color in the on-line version of the journal (http://www.springerlink.com).

Table 1. Selected bond lengths (*d*) in the complexes

Compound	*d*/Å			
	M^I—O	Co^{II}—O	M^I...Co	N—O
1	2.205(6)—2.350(6)	1.991(5)—2.198(6)	3.052(3)	—
2	2.293(7)—2.541(3)	2.063(3)—2.073(3)	3.429(2), 3.435(2)	—
2a	2.629(7)—2.825(3)	2.054(3)—2.094(3)	3.707(2), 3.716(2)	—
3		2.004(2)—2.169(2)		—
	Co^{III}—O	Co^{II}—O	Co...Co	
4	1.872(4)—1.918(4)	1.979(4)—2.208(5)	2.791(2)—2.950(1)	—
5	1.868(6)—1.941(6)	2.023(6)—2.156(6)	2.744(2)—2.896(2)	—
6	1.859(4)—1.969(4)	2.042(5)—2.219(4)	2.746(2)—2.954(2)	—
7	1.867(4)—1.929(3)	2.002(4)—2.273(3)	2.824(2)—2.968(2)	1.286(6), 1.287(8)
8	1.868(3)—1.921(3)	1.977(3)—2.286(3)	2.808(2)—2.951(1)	1.303(5), 1.292(8)
9	1.869(5)—1.923(5)	2.010(6)—2.226(5)	2.805(2)—2.960(2)	1.271(10), 1.309(14)
10	1.877(5)—1.910(5)	1.996(6)—2.241(5)	2.797(2)—2.993(2)	1.280(9), 1.278(11)
11	1.869(4)—1.922(4)	1.983(4)—2.200(4)	2.798(2)—2.953(1)	1.328(7), 1.270(9)
12	1.884(2)—1.920(2)	1.995(2)—2.233(2)	2.8047(8)—2.9571(6)	1.277(4)

The use of the dinuclear pivalate complex $[Co_2(Piv)_4(HPiv)_4(H_2O)]$ as the starting compound,[13] which is also readily soluble in low-polarity solvents, in the reaction with $Co(hfac)_2$ resulted in the formation of the tetranuclear mixed-ligand complex $[Co_4(Piv)_4(hfac)_2(OH)_2(HPiv)_4] \cdot HPiv$ (**3**) containing both Piv and hfac anions in the ligand shell. The highest yield of **3** was achieved with the use of the reagent ratio $\{Co_2\} : Co(hfac)_2 = 3 : 2$. This fact is consistent with the equation of the reaction

$$3\,[Co_2(Piv)_4(HPiv)_4(H_2O)] + 2\,[Co(hfac)_2 \cdot 2H_2O] =$$
$$= 2\,[Co_4(Piv)_4(hfac)_2(OH)_2(HPiv)_4] \cdot HPiv + 6\,HPiv + 3\,H_2O.$$

In molecule **3**, the coordination polyhedra of the Co(3) and Co(4) atoms can be described as distorted octahedra formed by O atoms of three bridging Piv anions, the μ_3-OH group, and two HPiv molecules (Fig. 3, *a*). The octahedral environment of the Co(1) and Co(2) atoms

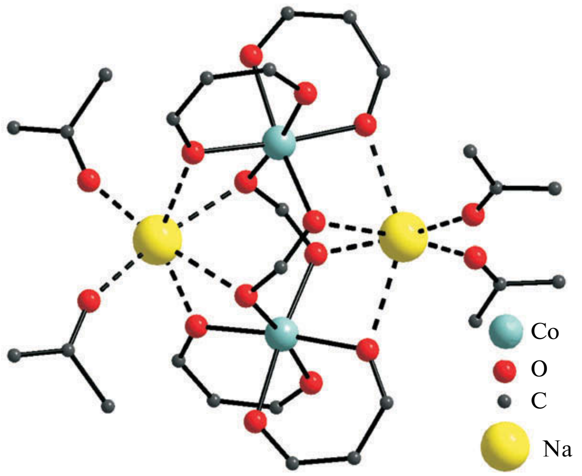

Fig. 2. Structure of ionic associate **2**. The H atoms and the Bu^t and CF_3 groups are not shown.

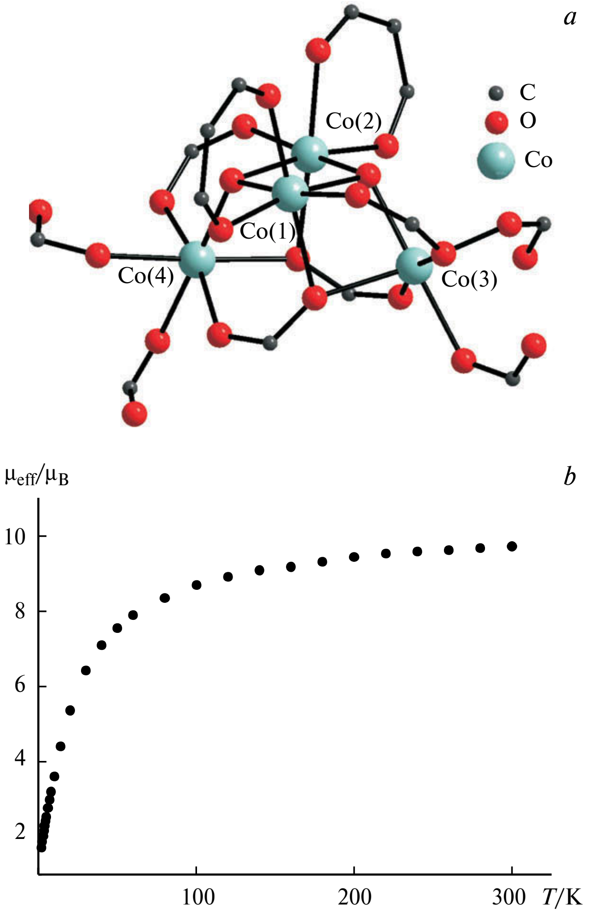

Fig. 3. Molecular structure (*a*, the H atoms and the Bu^t and CF_3 groups are not shown) and the experimental plot $\mu_{eff}(T)$ for **3** (*b*).

is formed by O atoms of two μ_3-OH groups, two bridging Piv anions, and the hfac anions coordinated in a bidentate fahsion. The Co—O distances are in the range of 2.004(2)—2.169(2) Å.

The high-temperature effective magnetic moment (μ_{eff}) for **3** (9.7 μ_B at 300 K) is substantially larger than the calculated electron magnetic moment (7.74 μ_B) for four noninteracting Co^{II} ions with the spin 3/2 and g = 2, which is well known to be due to the orbital contribution (see Fig. 3, *b*). Based on the average magnetic moment determined for a broad spectrum of high-spin octahedral Co^{II} complexes (4.95 μ_B),[14] the smallest high-temperature limit approached by the magnetic moment of the system consisting of four noninteracting high-spin Co^{II} ions with g = 2 should be 9.9 μ_B, which is consistent with the experimental data (see Fig. 3, *b*).

The reaction of the hexanuclear complex $[Co^{II}_4Co^{III}_2(O)_2(Piv)_{10}(H_2O)(THF)_3]$ (see Ref. 15) with $Co(hfac)_2$ affords the mixed-ligand tetradecanuclear complex $[Co^{III}_4Co^{II}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2HPiv \cdot 2H_2O \cdot 3C_7H_{16}$ (**4**) (Fig. 4, *a*). The $\{Co^{III}_4O_2\}$ moiety typical of polynuclear cobalt pivalates[13] is located in the center of the centrosymmetric metal-oxygen core (see Fig. 4, *b*). Due to the shortest Co—O distances, we assigned the oxidation state 3+ to the cobalt ions of these moieties. The Co^{III}—O and Co^{II}—O distances are 1.872(4)—1.918(4) and 1.979(4)—2.208(5) Å, respectively (see Table 1). The experimental plot $\mu_{eff}(T)$ for complex **4** is shown in Fig. 4, *c*. Nowadays, the theoretical analysis of the corresponding plots for polynuclear cobalt compounds cannot be performed.[16] It can only be speculated that antiferromagnetic exchange interactions predominate in the solid state of **4**, which leads to a decrease in μ_{eff} as the temperature is decreased.

It should be noted that, as expected, the dissolution of **4** in polar solvents (for example, in alcohols) leads to the transformation of the tetradecanuclear molecule. For example, an analysis of the structure of single crystals, which were obtained after the recrystallization of **4** from MeOH, revealed that compound **4** is transformed into the hexa- and octanuclear Piv hfac complexes $[Co_6(Piv)_6(hfac)(O)_2(MeO)_4(H_2O)(MeOH)_2] \cdot 2MeOH$ (**5**) and $[Co_8(Piv)_6(hfac)_2(O)_2(MeO)_8(MeOH)_2] \cdot 2H_2O$ (**6**), respectively (Fig. 5). We failed to develop procedures for the synthesis of these compounds in large amounts.

The metal core of these compounds is based on the distorted cubane moiety $\{Co_4O_4\}$. Two such moieties form the metal-oxygen cage $[Co^{III}_3Co^{II}_3(Piv)_6(hfac)(O)_2(MeO)_4(H_2O)(MeOH)_2]$ by sharing a face (see Fig. 5, *a*), and the moieties linked by μ_2-OMe bridges form $[Co^{III}_4Co^{II}_4(Piv)_6(hfac)_2(O)_2(MeO)_8(MeOH)_2]$ (see Fig. 5, *b*). As can be seen from Fig. 5, these compounds are characterized by the incorporation of the O atoms of the μ_3-bridging MeO anions into the metal-oxygen core. The coordination environment of all Co atoms can be described as slightly distorted octahedra; the Co—O distances are 1.859(4)—1.969(4) Å for Co^{III} and 2.023(6)—2.219(4) Å for Co^{II}.

Previously, it has been shown[17] that the reaction of $[Co_6(O)_2(Piv)_{10}(THF)_3H_2O] \cdot 1.5THF$ with 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (NIT-Me) leads to the transformation of both the polymetallic moiety $\{Co_6(O)_2(Piv)_{10}\}$ and the starting nitroxide as a result of redox reactions. The reaction

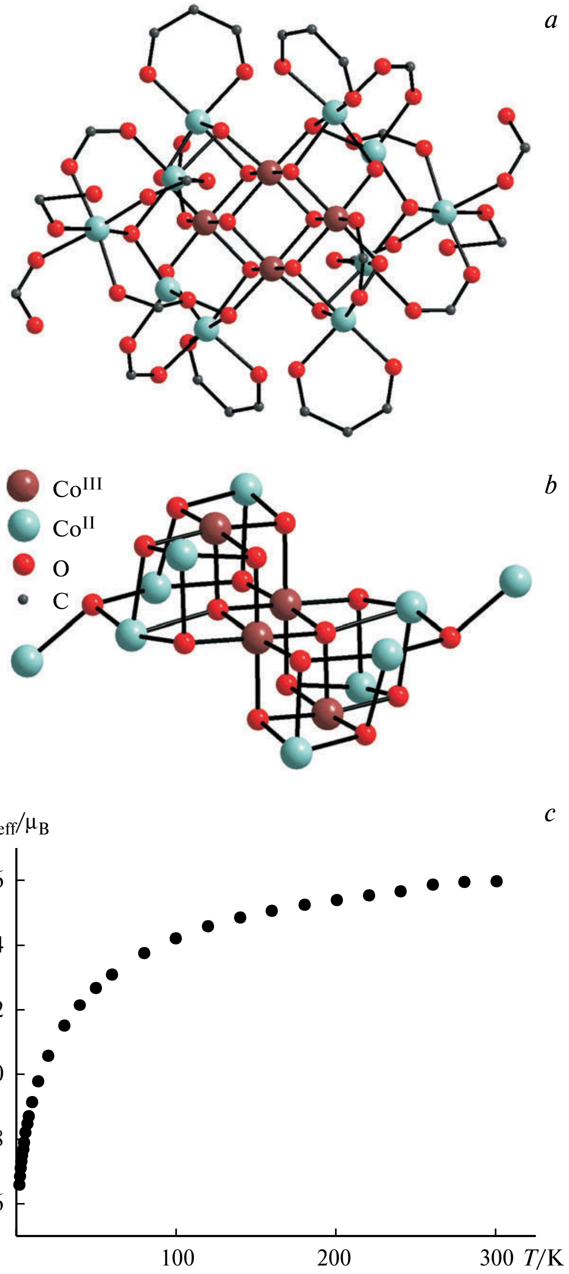

Fig. 4. Molecular structure of **4** (*a*, the H atoms and the Bu^t and CF_3 groups are not shown), the structure of the metal-oxygen core (*b*), and the experimental plot $\mu_{eff}(T)$ for **4** (*c*). The Co^{III} ions of this fragment are shown in brown.

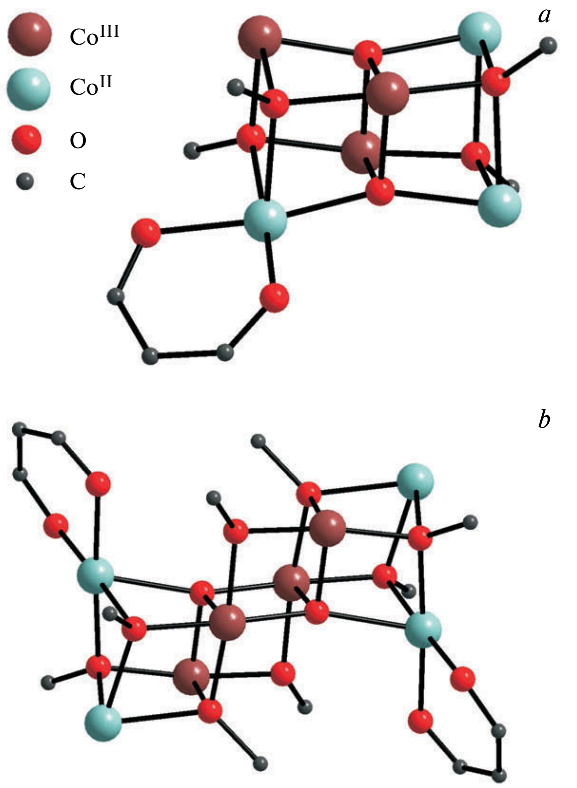

Fig. 5. Structures of the metal cores in $[Co_6(Piv)_6(hfac)(O)_2(MeO)_4(H_2O)(MeOH)_2]$ (**5**) (*a*) and $[Co_8(Piv)_6(hfac)_2(O)_2(MeO)_8(MeOH)_2]$ (**6**) (*b*).

of **4** with nitroxides was not accompanied by these transformations.

It was found that the tetradecanuclear compound has the unusual ability to precipitate nitroxides from solution. As a result, we obtained the following new heterospin crystalline solids: $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_4(NIT\text{-}H)_2] \cdot 4HPiv \cdot 2H_2O$ (**7**), $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_2(HPiv)_2] \cdot 2NIT\text{-}Me \cdot 2HPiv \cdot C_6H_{14}$ (**8**), $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2NIT\text{-}Et \cdot 2CHCl_3$ (**9**), $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2NIT\text{-}Ph \cdot 2C_6H_{14}$ (**10**), $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2L^1 \cdot 2CH_2Cl_2$ (**11**), and $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2L^2 \cdot C_6H_{14}$ (**12**), where NIT-H, NIT-Me, NIT-Et, and NIT-Ph are 2-imidazoline nitroxides, L^1 is 3-imidazoline nitroxide, and L^2 is di-*tert*-butyl nitroxide.

Some of these compounds, *viz*., **8**—**12**, were isolated in yields higher than 90% (see the Experimental section). This can, in principle, provide the basis for the development of an original procedure for the quantitative precipitation of nitroxides with the use of polynuclear compounds. The heterospin tetradecanuclear compounds are virtually structurally identical; only one of these compounds (**8**) differs from the other in that it contains coordinated HPiv molecules.

The X-ray diffraction study of the compounds showed that the efficient binding of nitroxides occurs due to the specific arrangement of the μ_3-OH groups in the $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]$ molecule, which is spatially complementary for the formation of numerous hydrogen bonds with the nitroxide moiety. As an example, Fig. 6 shows the structure of the metal-oxygen core of the complex and its hydrogen binding with NIT-Me in the structure of $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_2(HPiv)_2] \cdot 2NIT\text{-}Me \cdot 2HPiv \cdot C_6H_{14}$. Other NIT-R (R = Et, Ph), as well as L^1 and L^2, are bound to the tetradecanuclear core in a similar fashion. As can be seen from Table 1, the involvement of the nitroxide moiety into the complex has no effect on the bond lengths in the polynuclear moiety. The N—O bond lengths (1.271(10)—1.309(14) Å) in the nitroxides are also typical of such compounds. The nitroxides are bound to the tetradecanuclear molecule by hydrogen bonds between the O atom of the N—O group and the coordinated OH groups. The hydrogen bond parameters are given in Table 2.

The structure of the complex $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_4(NIT\text{-}H)_2] \cdot 4HPiv \cdot 2H_2O$ (**7**) differs in that small NIT-H has less steric hindrance compared to the bulky NIT-R substituents, where R = Me, Et, or Ph, and is coordinated to the tetradecanuclear molecule in a monodentate fashion (Fig. 7, *a*). The $Co-O_{NO}$ distance is 2.039(4) Å. Formally, the structure of **7** can be derived from the structure of **8** by performing the ligand rearrangement (see Fig. 7, *b*). This rearrangement involves the transfer of the hfac ligand from Co(6) to the terminal Co(7) atom accompanied by the replacement of the HPiv molecule and the bridging Piv ligand that links the Co(7) and Co(3) atoms together. In this case, the Co(3) atom is coordinated by the O atom of the coordinated H_2O molecule instead of the O atom of the pivalate anion, and the Co(6) atom is coordinated by NIT-H and HPiv instead of

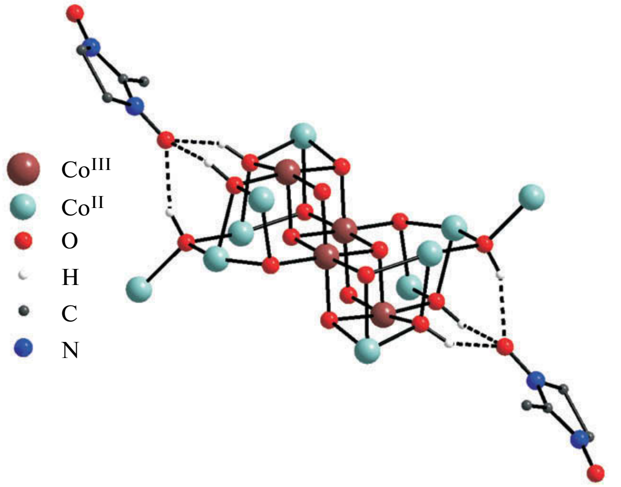

Fig. 6. Structure of the metal-oxygen core and the hydrogen bonds with NIT-Me in **8**.

Table 2. Hydrogen bond parameters

Compound	D—H...A	d(D—H)	d(H...A)	d(D...A)	DHA /deg
		Å			
8	O(5)—H(5A)—O(1R)	0.98	1.94	2.7334	135.9
	O(7)—H(7A)—O(1R)	0.98	2.10	3.0215	155.0
	O(8)—H(8A)—O(1R)	0.98	1.94	2.75650	139.3
9	O(4)—H(4)A)—O(1R)	0.98	2.09	3.00910	155.2
	O(6—H(6A)—O(1R)	0.98	1.90	2.7379	142.1
	O(8)—H(8A)—O(1R)	0.98	2.11	2.8519	131.3
10	O(3)—H(3)—O(1R)	0.99	2.19	3.1189	155.2
	O(4)—H(4)—O(1R)	0.99	2.17	2.9298	132.6
	O(5)—H(5)—O(1R)	0.99	1.91	2.7889	145.8
11	O(4W)—H(4)—O(1S)	0.99	2.24	2.9726	129.8
	O(5W)—H(5)—O(1S)	0.99	1.86	2.7467	147.2
	O(6W)—H(6)—O(1S)	0.99	2.22	3.1507	156.4
12	O(1W)—H(1)—O(1R)	0.99	2.32	3.2204	150.9
	O(2W)—H(2—O(1R)	0.99	1.90	2.7574	143.4
	O(5W)—H(5)—O(1R)	0.99	2.02	2.8084	135.0

hfac. The HPiv ligand forms a strong intramolecular hydrogen bond with the H_2O molecule coordinated to Co(3). The NIT-Me ligand is exchanged for NIT-H. An analysis of the molecular structure of **7** represented as the space-filling model (see Fig. 7, *c*) shows that the replacement of NIT-H by NIT-Me and NIT-R containing bulkier substituents R (Et, Ph) leads to the impermissible overlap between the R substituent and the Bu^t groups from the ligand environment of the polymetallic core (see Fig. 7, *c*) due to the absence of the free space for the methyl group. This hinders the coordination of NIT-R. This fact is confirmed also by calculations of the model geometry. Thus, the real distances from the C atom in position 2 of the imidazole ring to the nearest C atom of the Bu^t group upon the coordination of the nitroxide allow the "bulk" arrangement only of H atoms. There is not enough space for the Me group. The calculations showed also that NIT-H cannot serve as a bridge for steric reasons. Bulkier R groups cannot serve as bridges all the more. Consequently, NIT-R molecules cannot be used for the cross-

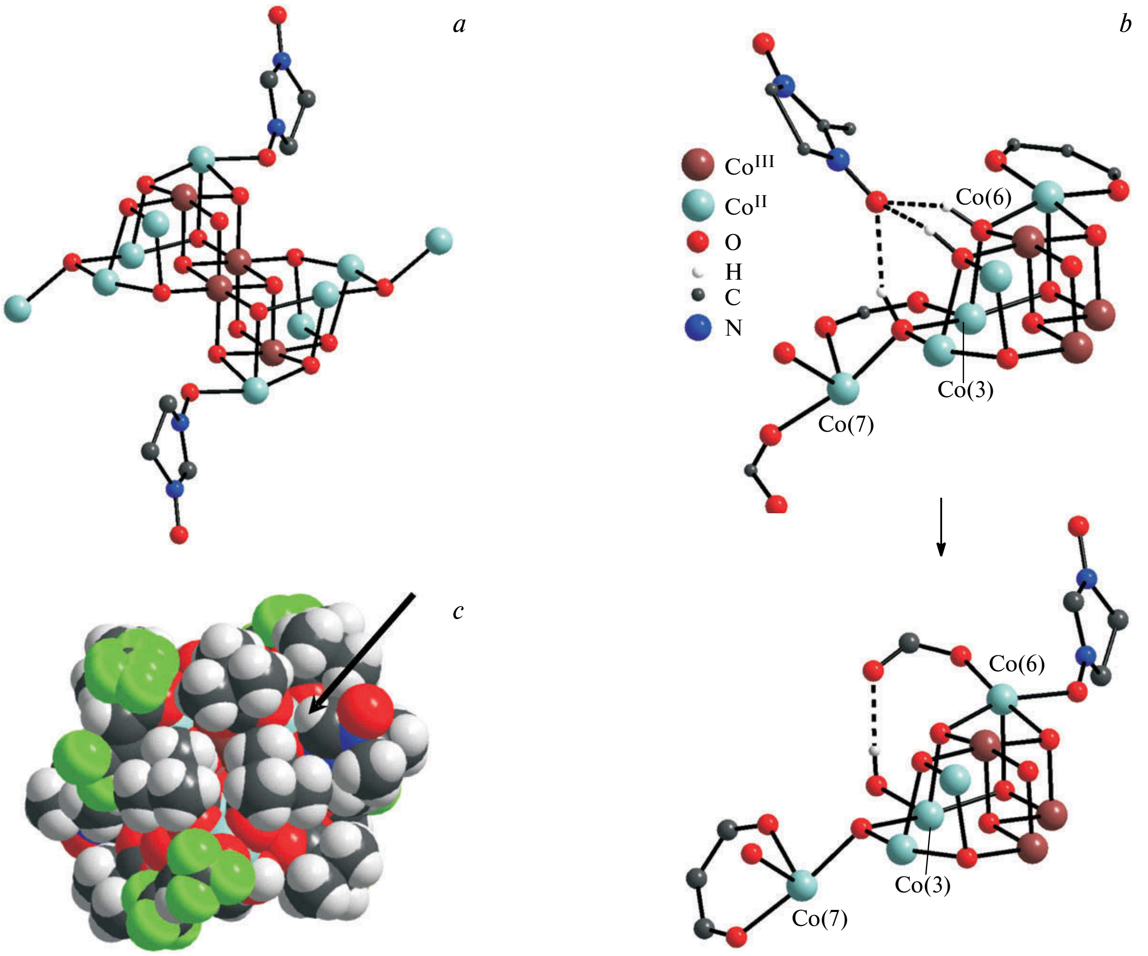

Fig. 7. Structure of the metal-oxygen core and the coordination of NIT-H in **7** (*a*); the scheme of the ligand rearrangement (*b*); the space-filling model of the structure of **7** (*c*); the H(R) atom, whose replacement by the Me group would lead to the impermissible overlap with the Bu^t groups of the polymetallic moiety, is indicated by an arrow.

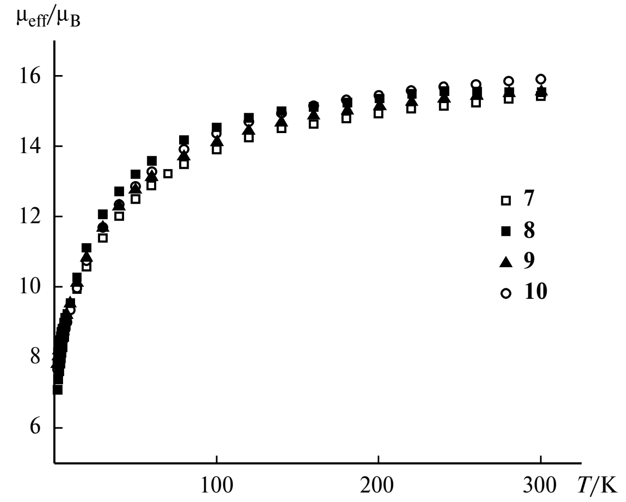

Fig. 8. Plot $\mu_{eff}(T)$ for complexes **7**—**10**.

linking of the tetradecanuclear moieties under consideration to form heterospin high dimensional compounds.

The investigation of the magnetic properties of compounds **7**—**10** showed that antiferromagnetic exchange interactions predominate in the polynuclear moieties, resulting in a decrease in μ_{eff} as the temperature is decreased. The high-temperature magnetic moments μ_{eff} for **7**—**10** have similar values (15.4, 15.5, 15.5, and 15.9 μ_B, respectively; Fig. 8), *i.e.*, they tend to the limit 16 μ_B,[16] which can be estimated based on the average value of 4.95 μ_B for ten Co^{II} ions.

Therefore, our study showed that cobalt pivalates can be used in the reaction with $Co(hfac)_2$ for the synthesis of polynuclear mixed-ligand Piv hfac compounds. The latter are readily soluble in many organic solvents and can be used in further reactions with the aim of synthesizing heterospin complexes with nitroxides. It was found that the tetradecanuclear mixed-ligand Piv hfac compound has an unusual ability to precipitate nitroxides, which contain no donor fragments other than $O^{\cdot}$—N<, from solution. The efficient binding of nitroxides is facilitated by the specific arrangement of the μ_3-OH groups in the $[Co_{14}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]$ molecule, which is spatially complementary for the formation of numerous hydrogen bonds with the nitroxide moiety.

Experimental

***catena*-Tetrakis[μ_3-(2,2-dimethylpropionato-*O,O,O´*)]tetrakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]di(μ_3-hydroxo)tetraethanoltetracobalt(II)disodium, $[Na_2Co_4(OH)_2(Piv)_8(EtOH)_4]$ (1).** The compound NaPiv (3.38 g, 27.2 mmol) was dissolved in EtOH (15 mL) with magnetic stirring and heating to 50 °C. A solution of $CoCl_2$ (0.7 g, 5.4 mmol) in EtOH (5 mL) was added with stirring to the cooled reaction solution. Sodium chloride that precipitated was filtered off, and the filtrate was kept in an open flask at room temperature for 2 weeks, during which the volume of the solution decreased by approximately a factor of two. The pink elongated-prismatic crystals that formed were filtered off, washed with cold EtOH, and dried in air. The yield was 0.46 g (30%). Found (%): C, 43.2; H, 7.1. $C_{22}H_{43}Co_2NaO_{10}$. Calculated (%): C, 43.4; H, 7.1.

Tetraacetone[μ_4-(2,2-dimethylpropionato-*O,O,O´,O´*)]tetrakis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)dicobalt(II)disodium, $[Na_2Co_2(hfac)_4(Piv)_2(Me_2CO)_4]$ (2). A solution of $Co(hfac)_2 \cdot 2H_2O$ (0.15 g, 0.3 mmol) in acetone (2 mL) was added to a filtered solution of $[NaCo_2(OH)(Piv)_4(EtOH)_2]$ (0.2 g, 0.3 mmol) in acetone (4 mL) at room temperature, and then heptane (4 mL) was slowly added. The reaction solution was kept in an open flask under ambient conditions for 4—5 days. Red crystals suitable for X-ray diffraction study were obtained. The crystals were filtered off and dried in air. The yield was 0.05 g (23%). Found (%): C, 31.9; H, 2.2. $C_{33}H_{28}Co_2F_{24}Na_2O_{13}$. Calculated (%): C, 31.6; H, 2.3. Complexes **2** and $[K_2Co_2(hfac)_4(Piv)_2(Me_2CO)_4]$ were formed after mixing NaPiv (KPiv) and $Co(hfac)_2 \cdot 2H_2O$ in a ratio of 1 : 1 in an acetone—heptane mixture, but the isolation of the pure product was complicated by an admixture of $Co(hfac)_2 \cdot 2H_2O$ crystals.

Tetrakis(2-carboxy-2-methylpropane)bis[μ_2-(2,2-dimethylpropionato-*O,O´*)]bis[μ_3-(2,2-dimethylpropionato-*O,O,O´*)]-bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)di(μ_3-hydroxo)-tetracobalt(II) 2-carboxy-2-methylpropane solvate, $[Co_4(Piv)_4(hfac)_2(OH)_2(HPiv)_4] \cdot HPiv$ (3). A solution of $Co(hfac)_2 \cdot 2H_2O$ (0.072 g, 0.14 mmol) in acetone (2 mL) and then heptane (5 mL) were added to a filtered solution of $[Co_2(Piv)_4(H_2O)(HPiv)_4]$ (0.2 g, 0.21 mmol) in acetone (2 mL) at room temperature. The solution was kept in an open flask at room temperature for 10 days. Claret prismatic crystals suitable for X-ray diffraction study were obtained. The crystals were filtered off and dried in air. The yield was 0.094 g (85%). Found (%): C, 41.1; H, 5.6; F, 14.3. $C_{55}H_{90}Co_4F_{12}O_{24}$. Calculated (%): C, 41.3; H, 5.7; F, 14.3.

Tetrakis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)tetrakis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)di(μ_3-oxo)tetracobalt(III)decacobalt(II) dihydrate tris(heptane) and bis(2-carboxy-2-methylpropane) solvate, $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2HPiv \cdot 2H_2O \cdot 3C_7H_{16}$ (4). A solution of $Co(hfac)_2 \cdot 2H_2O$ (0.176 g, 0.34 mmol) in acetone (3 mL) was added to a filtered solution of $[Co_6(O)_2(Piv)_{10}(H_2O)(THF)_3] \cdot 1.5$ THF (0.6 g, 0.34 mmol) in heptane (12 mL) at room temperature. The reaction solution was kept in an open flask at room temperature for 2—3 days. The brown prismatic crystals that formed were filtered off and dried in air. The yield was 0.2 g (29%). Found (%): C, 35.1; H, 4.9; F, 13.1. $C_{107}H_{188}Co_{14}F_{24}O_{58}$. Calculated (%): C, 34.9; H, 5.1; F, 12.4.

Tetraaquabis(4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) dihydrate tetrakis(2-carboxy-2-methylpropane) solvate, $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_4(NIT\text{-}H)_2] \cdot 4HPiv \cdot 2H_2O$ (7). A mixture of $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4] \cdot 2HPiv \cdot 2H_2O \cdot 3C_7H_{16}$ (0.033 g, 0.0085 mmol) and NIT-H (0.0027 g, 0.017 mmol) was dissolved in a mixture of hexane (4 mL) and $CHCl_3$ (2 mL). The reaction solution was filtered and kept for several days in a refrigerator (4°C). After 3—4 days. Brown elongated-prismatic crystals suitable for X-ray diffraction study were obtained. The crystals were filtered off and dried in air. The yield was 0.017 g (55%). Found (%): C, 32.7; H, 4.6; N, 1.1; F, 12.0. $C_{116}H_{182}Co_{14}F_{24}N_4O_{56}$. Calculated (%): C, 33.2; H, 4.9; N, 1.5; F, 12.1.

Bis(2,4,4,5,5-pentamethyl-2-imidazoline-3-oxide-1-oxyl)diaquabis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) hexane and bis(2-carboxy-2-methylpropane) solvate, $[Co_4^{III}Co_{10}^{II}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(H_2O)_2(HPiv)_2]\cdot 2(NIT\text{-}Me)\cdot 2HPiv\cdot C_6H_{14}$ (8). A solution of NIT-Me (0.0014 g, 0.0082 mmol) in hexane (2 mL) was gradually added through a filter to a filtered solution of $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2HPiv\cdot 2H_2O\cdot 3C_7H_{16}$ (0.016 g, 0.0041 mmol) in a mixture of $CHCl_3$ (1 mL) and hexane (2 mL) at room temperature. After storage of the reaction mixture for 3—4 days, prismatic crystals suitable for X-ray diffraction study were obtained. The crystals were filtered off and dried in air. The yield was 0.012 g (92%). Found (%): C, 34.5; H, 4.8; N, 1.1; F, 12.9. $C_{106}H_{182}Co_{14}F_{24}N_4O_{58}$. Calculated (%): C, 34.2; H, 4.9; N, 1.5; F, 12.3.

Bis(2-ethyl-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl)tetrakis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) bis(trichloromethane) solvate, $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2(NIT\text{-}Et)\cdot 2CHCl_3$ (9). A solution of NIT-Et (0.003 g, 0.016 mmol) in $CHCl_3$ (0.5 mL) was gradually added through a filter to a filtered solution of $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2HPiv\cdot 2H_2O\cdot 3C_7H_{16}$ (0.032 g, 0.0082 mmol) in $CHCl_3$ (2 mL) and hexane (4 mL) at room temperature. The subsequent work-up was carried out as described for **8**. The yield was 0.027 g (84%). Found (%): C, 34.9; H, 5.1; N, 1.4; F, 13.4. $C_{108}H_{182}Co_{14}F_{24}N_4O_{56}$. Calculated (%): C, 34.9; H, 4.9; N, 1.5; F, 12.3.

Bis(2-phenyl-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl)tetrakis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) bis(hexane) solvate $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2(NIT\text{-}Ph)\cdot 2C_6H_{14}$ (10). The procedure for the synthesis of compound **10** is similar to that used for the preparation of **9**, but the starting reactants were taken in triple amounts, and CH_2Cl_2 was used instead of $CHCl_3$. The yield was 0.094 g (94%). Found (%): C, 36.5; H, 4.9; N, 1.1; F, 12.0. $C_{116}H_{182}Co_{14}F_{24}N_4O_{56}$. Calculated (%): C, 36.6; H, 4.8; N, 1.5; F, 11.9.

Bis(2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl)tetrakis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) bis(dichloromethane) solvate, $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2L^1\cdot 2CH_2Cl_2$ (11). A solution of L^1 (0.0036 g, 0.016 mmol) in CH_2Cl_2 (1 mL) was gradually added to a filtered solution of $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2HPiv\cdot 2H_2O\cdot 3C_7H_{16}$ (0.0316 g, 0.008 mmol) in CH_2Cl_2 (1 mL) and hexane (4 mL) at room temperature. The reaction mixture was kept for one day. Brown elongated-prismatic crystals suitable for X-ray diffraction study were filtered off, washed with hexane, and dried in air. The yield was 0.028 g (87%). Found (%): C, 35.6; H, 4.9; N 1.0. $C_{118}H_{186}Cl_4Co_{14}F_{24}N_4O_{56}$. Calculated (%): C, 35.6; H, 4.7; N, 1.4.

Bis(di-*tert*-butyl nitroxide)tetrakis(2-carboxy-2-methylpropane)decakis[μ_2-(2,2-dimethylpropionato-*O,O´*)]tetradeca(μ_3-hydroxo)di(μ_3-oxo)tetrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tetracobalt(III)decacobalt(II) hexane solvate, $[Co^{III}{}_4Co^{II}{}_{10}(Piv)_{10}(hfac)_4(OH)_{14}(O)_2(HPiv)_4]\cdot 2L^2\cdot C_6H_{14}$ (12). The procedure for the synthesis of compound **12** is similar to that used for the preparation of **11**. The yield was 0.035 g (90%). Found (%): C, 35.9; H, 5.3; N, 0.7. $C_{112}H_{198}Co_{14}F_{24}N_2O_{54}$. Calculated (%): C, 36.2; H, 5.4; N, 0.8.

X-ray diffraction study. Single-crystal X-ray diffraction data sets were collected on a Bruker AXS SMART APEX CCD dif-

Table 3. Crystallographic parameters for compounds **1**—**6** and the X-ray diffraction data collection and structure refinement statistics

Parameter	**1**	**2**	**2a**	**3**	**4**	**5**	**6**
T/K	298	293	293	240	298	298	298
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
Z	4	4	4	2	1	4	4
a/Å	13.231(6)	24.1041(16)	24.415(8)	13.748(3)	19.645(2)	12.673(9)	15.200(13)
b/Å	18.979(8)	13.8826(9)	14.047(4)	13.759(3)	32.031(3)	23.620(17)	12.230(11)
c/Å	14.054(6)	22.6011(15)	22.286(7)	23.027(5)	28.382(3)	23.117(17)	21.98(2)
α/deg				89.148(3)			104.94(1)
β/deg	96.019(9)	119.483(1)	118.353(5)	80.112(3)	94.983(2)	103.92(2)	
γ/deg				61.281(3)			
V/Å^3	3510(3)	6583.6(8)	6726(4)	3751.8(13)	17791(3)	6717(9)	3948(6)
d_{calc}/g cm^{-3}	1.239	1.439	1.441	1.415	1.450	1.453	1.575
θ-Scan range/deg	1.81—23.33	1.76—23.29	1.73—23.31	1.69—23.65	1.22—23.33	1.69—23.55	2.22—23.30
I_{hkl} (meas./independent)	27011/5075	25130/4742	25130/4743	28404/10628	68766/12831	50233/9722	28481/5603
R_{int}	0.1535	0.0907	0.1108	0.0281	0.1386	0.1234	0.0794
Refined parameters	335	515	471	953	998	722	451
R_1	0.0861	0.0660	0.0530	0.0431	0.0687	0.0836	0.0728
wR_2 ($I > 2\sigma_I$)	0.1824	0.1437	0.1470	0.1221	0.1569	0.1978	0.1720
R_1	0.1448	0.1087	0.0882	0.0517	0.1180	0.1318	0.0961
wR_2 (all data)	0.2095	0.1624	0.1651	0.1289	0.1770	0.2181	0.1824

Table 4. Crystallographic parameters for compounds **7**—**12** and the X-ray diffraction data collection and structure refinement statistics

Parameter	**7**	**8**	**9**	**10**	**11**	**12**
T/K	240(2)	298	298	240	240	240
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	1	1	2	1	2	2
a/Å	17.236(3)	15.323(2)	19.0948(14)	16.242(6)	18.916(3)	16.1535(7)
b/Å	17.356(4)	17.852(3)	28.690(2)	18.073(7)	28.664(4)	16.2719(8)
c/Å	17.681(4)	18.283(3)	18.4980(14)	19.116(7)	18.611(3)	19.3095(8)
α/deg	114.126(14)	67.893(3)		115.286(7)		67.106(2)
β/deg	95.817(16)	88.233(4)	116.547(2)	90.580(8)	116.694(10)	71.203(3)
γ/deg	118.405(13)	66.819(3)		116.472(8)		61.564(2)
V/Å^3	3947.4(14)	4219.0(10)	9065.2(12)	4400(3)	9016(2)	4052.3(3)
d_{calc}/g cm^{-3}	1.578	1.499	1.448	1.503	1.466	1.523
θ-Scan range/deg	1.56—26.37	1.73—23.37	1.39—23.35	1.22—23.37	1.42—28.33	2.01—28.00
I_{hkl} (meas./independent)	34334/15854	33034/12161	70004/13072	34624/12715	74265/21810	62394/19342
R_{int}	0.1406	0.1349	0.1657	0.0902	0.2443	0.0542
Refined parameters	973	955	961	1020	998	1058
R_1	0.0653	0.0848	0.0801	0.0710	0.0673	0.0448
wR_2 ($I > 2\sigma_I$)	0.1142	0.2127	0.1626	0.1583	0.1376	0.1185
R_1	0.1362	0.1622	0.1576	0.1273	0.1792	0.0787
wR_2 (all data)	0.1528	0.2477	0.1896	0.2010	0.2490	0.1341

fractometer (Mo-Kα, $\lambda = 0.71073$ Å, absorption corrections were applied with the use of the Bruker SADABS software, version 2.10). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms were positioned geometrically and refined isotropically using the rigid-group approximation. All calculations associated with the structure solution and refinement were carried out with the use of the Bruker Shelxtl software (Version 6.14). Selected bond lengths and hydrogen bond parameters are listed in Tables 1 and 2, respectively. Crystallographic parameters and the X-ray diffraction data collection and structure refinement statistics are given in Tables 3 and 4.

Magnetic properties of the compounds were measured on a MPMS*XL* SQUID magnetometer (Quantum Design) in the temperature range 2—300 K and a magnetic field of 5 kOe. The paramagnetic terms of the magnetic susceptibility χ were evaluated taking into account the diamagnetic contribution, which was estimated from the Pascal constants. The effective magnetic moment was calculated by the equation

$$\mu_{\text{eff}} = \left(\frac{3k}{N_{\text{A}}\beta^2}\chi T\right)^{1/2} \approx (8\chi T)^{1/2},$$

where N_{A} is Avogadro's number, β is the Bohr magneton, and k is the Boltzmann constant.

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References

1. V. Ovcharenko, E. Fursova, G. Romanenko, V. Ikorskii, *Inorg. Chem.*, 2004, **43**, 3332.
2. E. Fursova, V. Ovcharenko, K. Nosova, G. Romanenko, V. Ikorskii, *Polyhedron*, 2005, **24**, 2084.
3. K. Nakata, H. Miyasaka, F. Iwahori, K. Sugiura, M. Yamashita, *Polyhedron*, 2005, **24**, 2250.
4. V. Ovcharenko, E. Fursova, G. Romanenko, I. Eremenko, E. Tretyakov, V. Ikorskii, *Inorg. Chem.* 2006, **45**, 5338.
5. E. Fursova, O. Kuznetsova, V. Ovcharenko, G. Romanenko, V. Ikorskii, I. Eremenko, A. Sidorov, *Polyhedron*, 2007, **26**, 2079.
6. E. Yu. Fursova, V. I. Ovcharenko, *Ross. Khim. Zh. (Zh. Ross. Khim. Obshch. im. D. I. Mendeleeva*, 2009, **53**, 23 [*Mendeleev Chem. J.*, 2009, **53** (Engl. Transl.)].
7. G. V. Romanenko, E. Yu. Fursova, V. I. Ovcharenko, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 1 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, **58**, 1].
8. E. Yu. Fursova, O. V. Kuznetsova, G. V. Romanenko, A. S. Bogomyakov, V. I. Ovcharenko, *Izv. Akad. Nauk, Ser. Khim.*, 2010, 330 [*Russ. Chem. Bull.*, *Int. Ed.*, 2010, **59**, 337].
9. O. V. Kuznetsova, E. Yu. Fursova, V. I. Ovcharenko, G. V. Romanenko, A. S. Bogomyakov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 2156 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 2198].
10. E. Yu. Fursova, O. V. Kuznetsova, V. I. Ovcharenko, G. V. Romanenko, A. S. Bogomyakov, M. A. Kiskin, I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 1742 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 1805].
11. E. Yu. Fursova, O. V. Kuznetsova, V. I. Ovcharenko, G. V. Romanenko, A. S. Bogomyakov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1175 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 1198].

12. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko, I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1773 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1999, **48**, 1751].
13. G. Aromí, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G.A. Timco, R. E. P. Winpenny, *Chem. Eur. J.*, 2003, **9**, 5142.
14. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1966.
15. A. A. Sidorov, M. E. Nikiforova, E. V. Pakhmutova, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, I. L. Eremenko, I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1851 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 1920].
16. V. T. Kalinnikov, Yu. V. Rakitin, *Vvedenie v magnetokhimiyu* [*Introduction to Magnetochemistry*], Nauka, Moscow, 1980, 320 pp. (in Russian).
17. E. Fursova, O. Kuznetsova, V. Ovcharenko, G. Romanenko, V. Ikorskii, I. Eremenko, A. Sidorov, *Polyhedron*, **26**, 2007, 2079.

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