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Replacement of carboxylate bridges in polynuclear nickel pivalates with 2-hydroxy-6-methylpyridine anions

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The reaction of 2-hydroxy-6-methylpyridine (HL, **1**) with nonanuclear nickel trimethylacetate $Ni_9(OH)_6(OOCCMe_3)_{12}(HOOCCMe_3)_4$ (**2**) in MeCN with a ratio M : L = 1 : 1 under mild conditions (20 °C, 15 min) led to degradation of the metal core to form the hexanuclear complex $(HL)_2(\mu_2\text{-}HL)_2Ni_6(\mu_3\text{-}OH)_2(\mu_2\text{-}H_2O)_2(\mu\text{-}OOCCMe_3)_8(\eta\text{-}OOCCMe_3)_2$ (**3**). Further heating of **3** in acetonitrile at 80 °C for 4 h afforded the $(HL)Ni_6(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}L)_3(\mu,\eta^2\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)$ complex. The reaction with the use of a 2 : 1 THF—EtOH mixture instead of acetonitrile at 50 °C gave the decanuclear complex $[Ni_{10}(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_4(\mu\text{-}OOCCMe_3)_6(\mu_3,\eta^2\text{-}L)_6(EtOH)_6](H_2O)_2$, which is also produced from compounds **1** and **2** in ethanol. The structures of the resulting complexes were established by X-ray diffraction.

Key words: 2-hydroxy-6-methylpyridine, nickel complexes, X-ray diffraction study.

The formation of pivalate complexes is extensively used in chemistry to transfer transition metals to an organic medium, in which these compounds are, as a rule, readily soluble. These compounds can further be modified through interactions with various organic donor molecules by controlling the metal core structure in the resulting compounds based on the geometric and electronic features of both the starting pivalates and organic counter agents.[1—8] The bridging pivalate groups are also often involved in structural modifications, for example, through replacement with other organic anionic ligands.[8—12] 2-Hydroxypyridine can serve as a convenient modifying agent. In the free state, this compound exists predominantly as pyridone[13,14] and can either be coordinated as a neutral molecule or undergo deprotonation to give the 2-pyridonate anion. Apparently, the first step of the reaction with the transition metal ion involves coordination of 2-hydroxy-6-methylpyridine through the oxygen atom because the nitrogen atom is protonated. The further behavior of the transition metal—pyridone fragment depends on many factors, including the nature of other acido ligands bound to the metal center. The structures of the resulting complexes are determined to a great extent by the structure-forming role of the pyridonate anions, whose geometric characteristics are similar to those of the carboxylate ligands.[15—20] Pivalate complexes are attractive objects for attack by hydroxypyridine because the pivalate anionic ligands can easily bind a proton (pK_a of pivalic acid is 5.05) and can be released,[21] thus giving a place for a new bridge. In substitution reactions, the nature of the metal center is also of importance.

Recently, we have demonstrated that the reaction of polymeric cobalt pivalate with 2-hydroxy-6-methylpyridine (HL, **1**) gives the hexanuclear complex $Co_6(\mu_3\text{-}OH)_2(\eta^2,\mu_3\text{-}L)_2(\mu\text{-}OOCCMe_3)_8(HOOCCMe_3)_4$.[22] In the presence of an excess of HL, the pivalate ligands are further replaced to give the complex $(HL)Co_6(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}L)_3(\mu,\eta^2\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}$

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$\mathrm{OOCCMe_3}$). In the present study, we examined the reaction of **1** with the nonanuclear nickel(II) trimethylacetate complex $\mathrm{Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)(\mu_3\text{-}OH)_3(\mu_{\it n}\text{-}OOCCMe_3)_{12}}$ (**2**) containing 12 bridging different-dentate pivalate ligands.

Results and Discussion

The reaction of nonanuclear nickel trimethylacetate **2** with HL (**1**) in acetonitrile at room temperature led to degradation of the metal core and the formation of the hexanuclear complex $\mathrm{(HL)_2(\mu_2\text{-}HL)_2Ni_6(\mu_3\text{-}OH)_2(\mu_2\text{-}H_2O)_2(\mu\text{-}OOCCMe_3)_8(\eta\text{-}OOCCMe_3)_2}$ (**3**) (Scheme 1, Fig. 1, Table 1).

The X-ray diffraction study demonstrated that molecule **3** has a symmetrical structure, and the nickel atoms are linked together by both the bridging pivalate anions (Ni—O, 2.007(3)—2.168(2) Å) and the oxygen atom of 6-methyl-2-pyridone (Ni(1)—O(11), 2.135(3) Å; Ni(2)—O(11), 2.103(3) Å). In addition, complex **3** contains bridging hydroxy groups and water molecules (Ni—O(μ_3-OH), 1.961(2)—2.024(3) Å; Ni—O(μ_2-$\mathrm{OH_2}$), 2.115(3) and 2.126(3) Å). The peripheral nickel atoms are in an octahedral environment due to additional coordination by monodentate neutral pyridone molecules (Ni(1)—O(12), 2.066(3) Å).

However, under these conditions, only four HL ligands are involved in interactions with the starting complex **2**. The situation changes in the case of prolonged heating (M : L = 1 : 1), resulting in the formation of the hexanuclear complex $\mathrm{(HL)Ni_6(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}L)_3(\mu,\eta^2\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)}$ (**4**) (see Scheme 1, Fig. 2, and Table 1).

In complex **4**, the distances between all nickel atoms are nonbonded (Ni...Ni, 2.978(1)—3.764(1) Å) (see Fig. 1 and Table 1), and these atoms are linked to each other by five trimethylacetate bridges (Ni—O, 1.968(3)—2.216(3) Å), five tridentate bridging 2-pyridonate anions (Ni—N, 2.039(3)—2.089(3) Å; Ni—O, 2.013(3)—2.2285(3) Å), and the μ_3-OH group (Ni—OH, 1.971(3)—2.015(3) Å). In this complex, the Ni atoms are in an octahedral coordination environment, although one Ni—O distance to the Ni(2) atom is very long (O(17)—Ni(2), 2.470(3) Å). Two metal atoms are coordinated by nonbridging ligands. Thus, the Ni(6) atom is bound to the chelate pivalate group (Ni—O, 2.081(3) and 2.105(3) Å), and the Ni(4) atom is coordinated by the pyridone ligand (Ni(5)—O(13), 2.041(3) Å) (see Fig. 2). Therefore, upon the replacement of the trimethylacetate anions in complex **4** by pyridonate anions, the metal to ligand ratio becomes equal to 1 : 1, although one of the hydroxypyridine ligands remains neutral. Complex **4** is

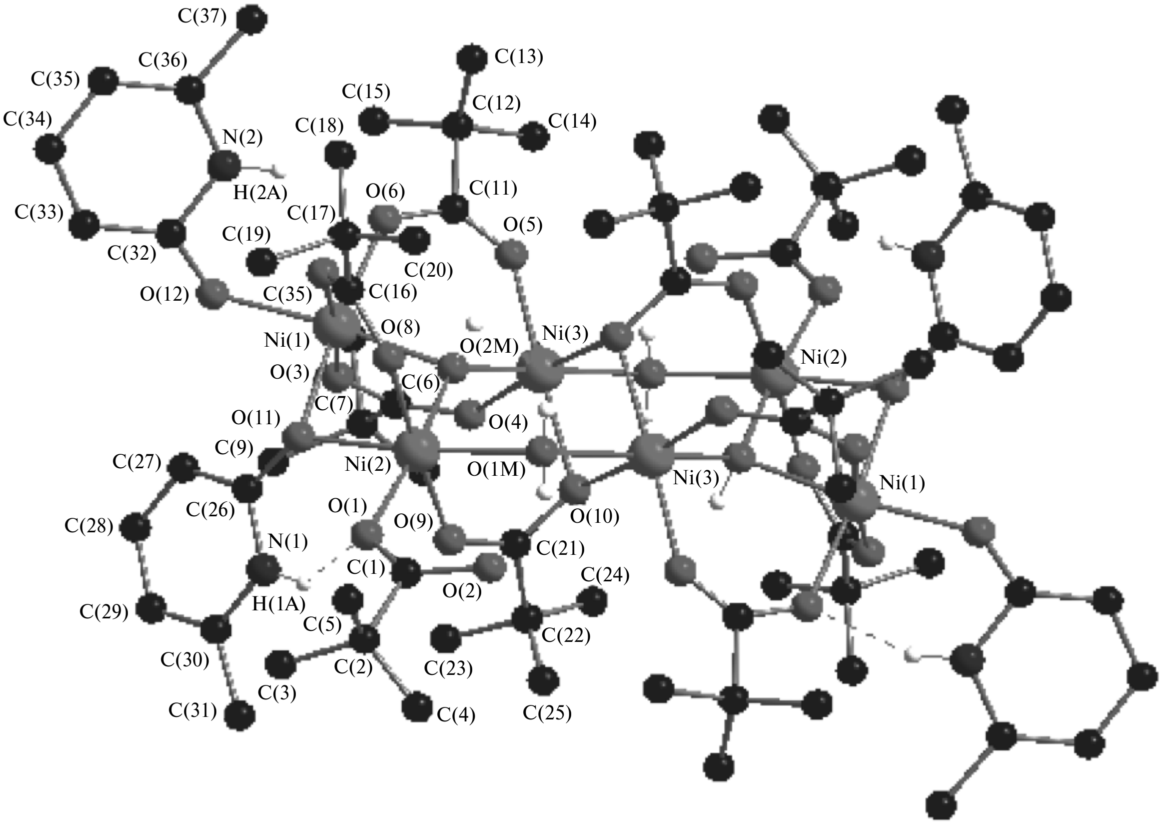
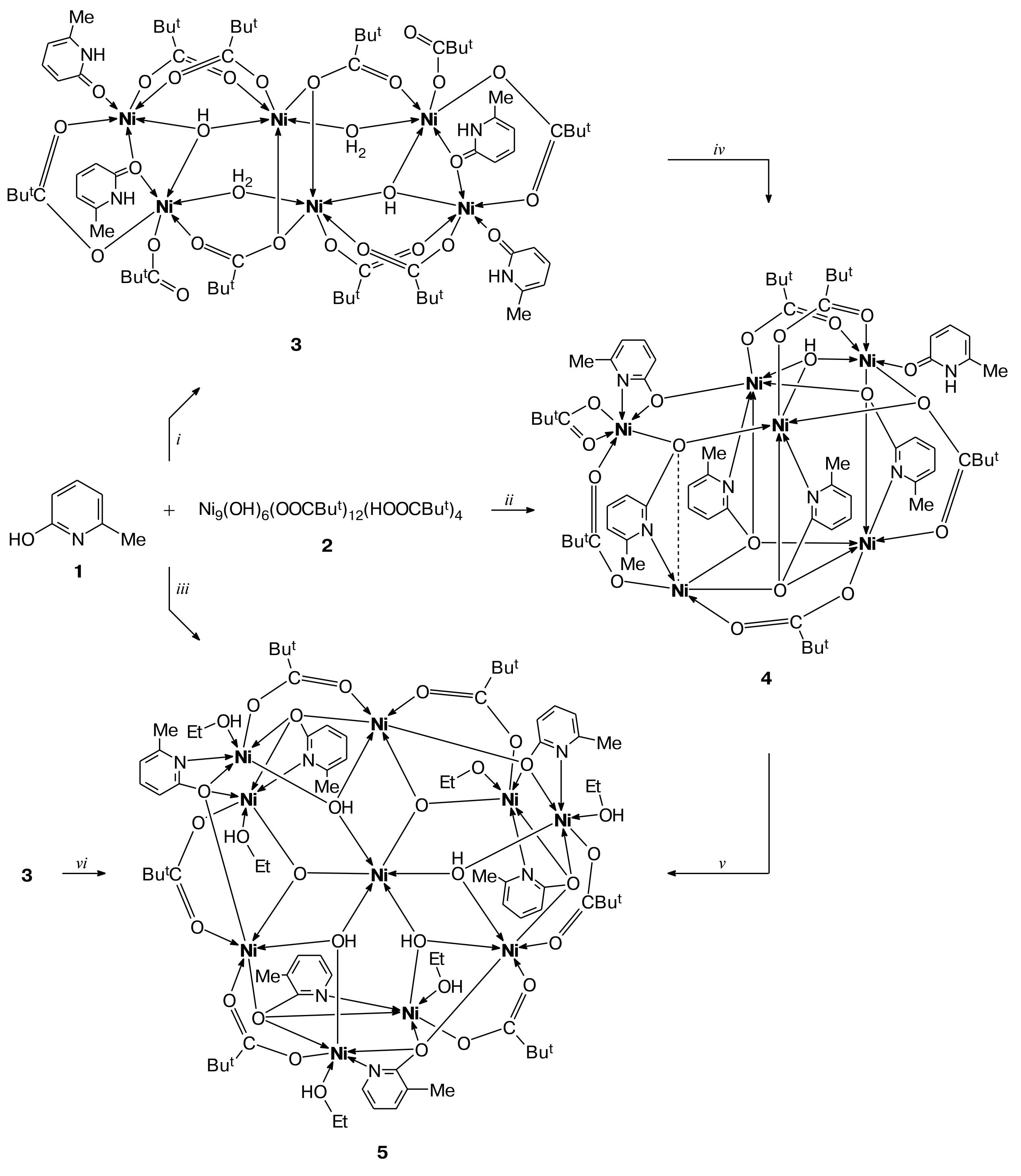


Fig. 1. Structure of complex **3**.

Scheme 1



Reagents and conditions: *i*. MeCN, $Ni_{at} : L = 1 : 1$, stirring of the solutions at ~20 °C; *ii*. MeCN, $Ni_{at} : L = 1 : 1$, 80 °C, 4 h; *iii*. EtOH, $Ni_{at} : L = 1 : 1$, 80 °C; *iv*. recrystallization from THF—MeCN; *v*. recrystallization from THF—EtOH, 70 °C; *vi*. THF—EtOH, 70 °C.

also formed upon heating of a solution of complex **3** in a 2 : 1 THF—MeCN solvent mixture at 60 °C for 30 min. Taking into account the different Ni : L ratios in complexes **3** (3 : 2) and **4** (1 : 1), low solubility of the complexes in MeCN, and low yields of the reaction products, it can be suggested that the solution con-

Table 1. Selected geometric characteristics of complexes **3—5**

Bond	d/Å		
	3	**4**	**5**
Ni_{cent}—O (μ_3-OH and μ_3-O)	—	—	2.038(12); 2.084(10)
Ni—O (μ_3-OH)	1.961(2)—2.024(3)	1.971(3)—2.015(3)	1.964(11)—2.106(11)
Ni—O (μ_2-OH_2)	2.115(3); 2.126(3)	—	—
Ni—O (μ_3-$OOCCMe_3$)	2.157(3)—2.168(2)	2.002(3)—2.216(3)	—
Ni—O ($OOCCMe_3$(bridge))	2.007(3)—2.071(3)	1.968(3)—2.037(3)	1.985(14)—2.04(2)
Ni—O ($OOCCMe_3$(chelate))	—	2.081(3); 2.105(3)	—
Ni—O ($OOCCMe_3$(terminal))	2.026(3)	—	—
Ni—N	—	2.039(3)—2.089(3)	2.025(16); 2.043(19)
Ni—O (L)	—	2.013(3)—2.285(3)	2.042(15)—2.245(13)
Ni—O (HL)	2.066(3)—2.135(3)	2.041(3)	—
Ni—O (EtOH)	—	—	2.097(14); 2.149(16)
Ni...Ni	3.063(3)—3.690(3)	2.978(1)—3.764(1)	3.052(4)—3.939(4)
O—H...O	1.70	—	—
N—H...O	2.04—2.15	—	—

tains other highly soluble products, which we failed to isolate.

The reaction with the use of ethanol instead of acetonitrile afforded the unusual decanuclear complex $Ni_{10}(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_4(\mu\text{-}OOCCMe_3)_6(\mu_3,\eta^2\text{-}L)_6(EtOH)_6$ (**5**), which was isolated as a solvate with two water molecules (see Scheme 1, Fig. 3, and Table 1).

According to the X-ray diffraction data, all nickel atoms are in an octahedral coordination environment, nine peripheral nickel atoms being linked to each other to

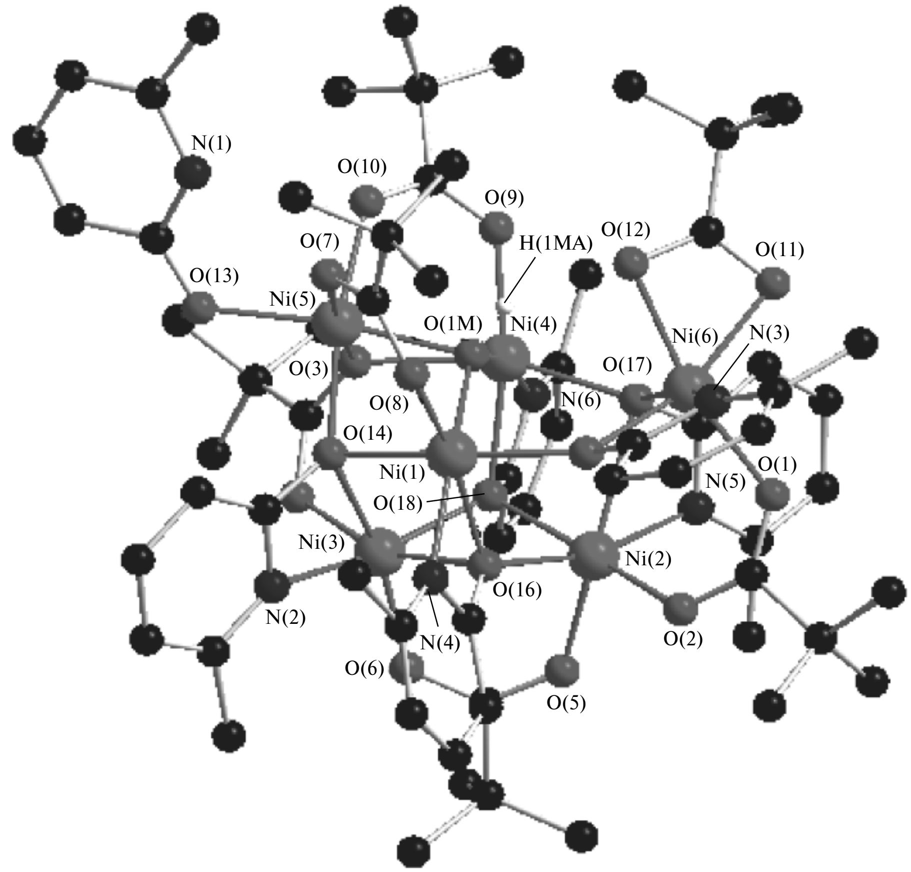


Fig. 2. Molecular structure of cluster **4**.

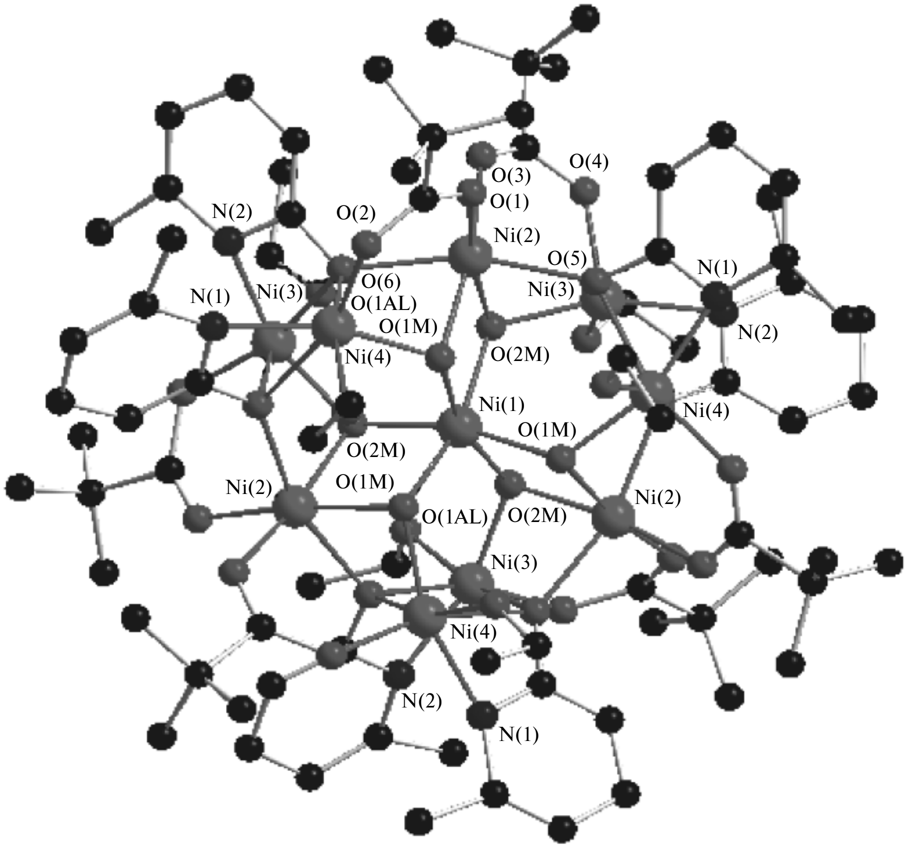


Fig. 3. Molecular structure of complex **5**.

form a closed symmetrical system due to the μ_3-O function of the oxygen atoms of the 6-methyl-2-pyridonate and carboxylate anions. The coordination environment of six out of nine peripheral nickel atoms is formed by the monodentate-coordinated ethanol molecule (Ni—O, 2.097(14) and 2.149(16) Å), the oxygen atom of the pivalate anion (Ni—O, 1.985(14)—1.999(14) Å), and the chelate 6-methyl-2-pyridonate anions (Ni—O, 2.042(15)—2.245(13) Å; Ni—N, 2.025(16)—2.043(19) Å). The oxygen atoms of the ligand and pivalate anions act as bridges between the other three nickel atoms (Ni—O are 2.148(14)—2.162(13) and 2.024(13)—2.04(2) Å for the 6-methyl-2-pyridonate and carboxylate anions, respectively). The molecule has crystallographic symmetry C_3; the threefold axis passes through the central Ni(1) atom. The coordination environment of this atom is formed by six equivalent oxygen atoms (Ni_{cent}—O, 2.038(12)—2.084(10) Å), which serve the bridging μ_3-O function to link this nickel atom to nine other nickel atoms (Ni—O, 1.964(11)—2.106(11) Å). Four of these oxygen atoms belong to hydroxy groups and only two oxygen atoms are involved in oxo bridges. As a result, the protons of four hydroxy groups in molecule **5** are disordered and can formally occupy all six positions (at the oxygen atoms) with an occupancy of 2/3.

Decanuclear cluster **5** exhibits antiferromagnetic properties, and its effective magnetic moment monotonically decreases from 9.607 to 5.229 μ_B (per molecule) in the temperature range of 300—2 K due to spin-spin exchange interactions (Fig. 4).

The presence of the polymetallic metal core with bridging ligands, which are prone to electron density delocalization, in complexes **3**, **4**, and **5**, as well as in the starting complex **2**, implies the possibility that such compounds containing a large number of nickel atoms have unusual electrochemical properties.

The cyclic voltammetry (CV) data for the compounds under study are given in Table 2. Oxidation of the decanuclear nickel complex involves two quasireversible one-electron steps (Fig. 5) at potentials of +1.05 and +1.532 V (see Table 2).

The reversibilities (I_c/I_a) (see Table 2) of the process provide evidence for the formation of rather stable intermediates under electrochemical experimental conditions.[23] The first redox transfer affords stable cationic complex $\mathbf{5}^+$. This is confirmed by the results of electrolysis at the controlled potential (+1.2 V). The cyclic voltammogram of cation $\mathbf{5}^+$ produced by electrolysis is no different from the initial voltammogram, which is evidence of reversible oxidation of complex **5**. The first re-

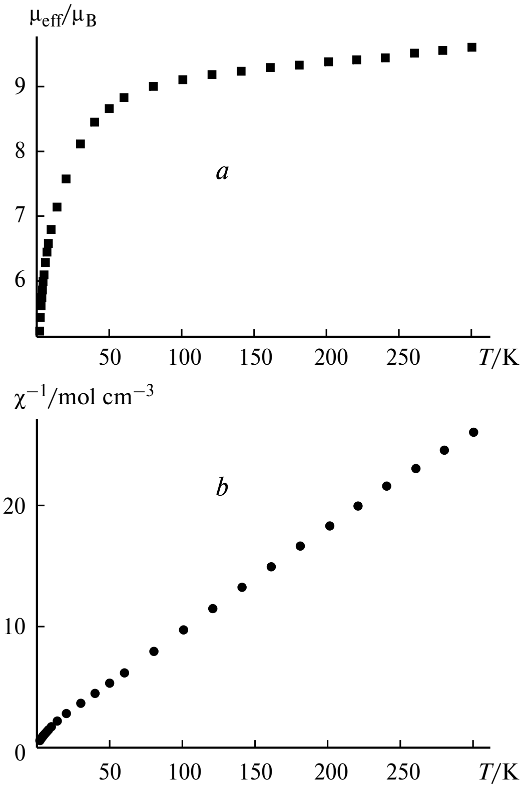


Fig. 4. Plots $\mu_{eff}(T)$ (*a*) and $1/\chi(T)$ (*b*) for compound **5**.

dox step occurs apparently in the inner coordination sphere of the complex, because the coordinated ethanol molecules and pivalate anions do not exhibit redox activity in this potential range.[24] Stability of cation $\mathbf{5}^+$ generated during oxidation indicates that delocalization of the effective charge can occur in the structure as a whole. The second quasireversible redox process observed at a more anodic potential (1.532 V) provides evidence for the possible formation of the dicationic complex. The formation of cation $\mathbf{5}^+$ in the first step accompanied by the internal electronic rearrangement does not allow us to reach a decisive conclusion regarding the electron-transfer center in the second redox transition. However, the observed partial reversibility of the process confirms the assumption that the metal carboxylate core is actively involved in the intramolecular charge transfer in these systems.

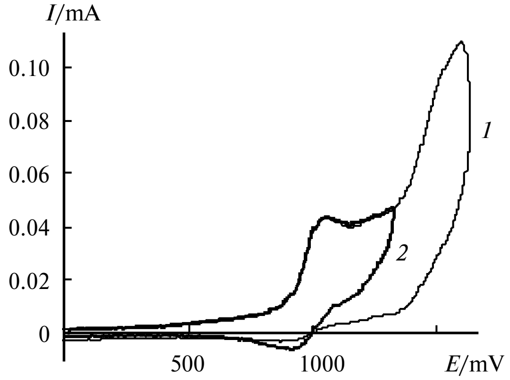


Fig. 5. CV data for oxidation of complex **5** in ranges of 0—1400 (*1*) and 0—1700 mV (*2*) (CH_2Cl_2, V = 0.2 V s^{-1}, Ag/AgCl, $C = 1 \cdot 10^{-3}$ mol L^{-1}, Pt electrode, 0.1 *M* Bu_4NClO_4).

The cyclic voltammograms of hexanuclear nickel complexes **3** and **4** show two irreversible oxidation peaks in the anodic region (Fig. 6).

Presumably, the first weakly pronounced peak corresponds to oxidation of the pivalate anion because similar potentials were obtained for potassium pivalate Me_3CCOOK under the same conditions (see Table 2). This indicates that dissolution of the complexes in DMF can lead to complete or partial removal of one of the

Table 2. Electrochemical potentials of the complexes[a]

Compound	E_{p1}^{ox}/V	I_c/I_a	*n*	E_{p2}^{ox}/V	I_c/I_a	*n*	E_{p1}^{red}/V	*n*
1 (HL)[b]	1.613	0.23	1	—	—	—	—	—
1[c]	1.627	—	2	—	—	—	−1.80	—
2[c]	1.713	>1	—	—	—	—	−1.55	>1
3[b]	0.963	—	—	1.598	—	>2	−1.670,	1
							−1.864	—
4[b]	0.923	—	—	1.555	—	>2	−1.656	—
5[c]	1.05	0.54	1	1.532	0.5	1	−1.325	1
Me_3CCOOK	0.966	—	—	—	—	—	—	—

[a] Conditions: a Pt electrode, V = 0.2 V s^{-1}, 0.1 *M* Bu_4NClO_4, $C = 3 \cdot 10^{-3}$ mol L^{-1}, the potentials are given with respect to Ag/AgCl.

[b] DMF.

[c] CH_2Cl_2.

Note: I_c/I_a is the ratio of the cathodic peak current to the anodic peak current (reversibility), *n* is the number of electrons involved in the electrochemical reaction compared to the current of the reference (ferrocene), E_{p1}^{ox} and E_{p2}^{ox} are the potentials of the first and second oxidation peaks, respectively, and E_{p1}^{red} is the potential of the first reduction peak.

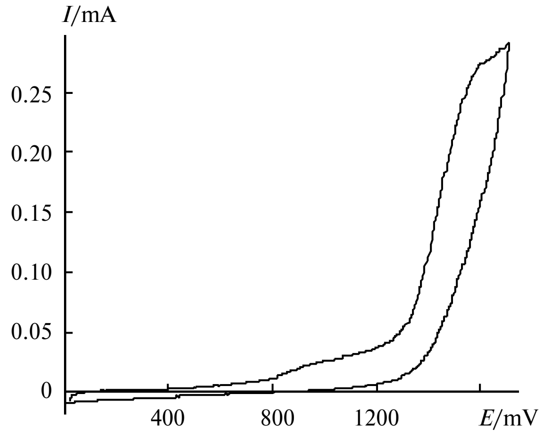


Fig. 6. CV data for oxidation of complex **3** (DMF, $V = 0.2$ V s^{-1}, Ag/AgCl, $C = 3 \cdot 10^{-3}$ mol L^{-1}, Ar, Pt electrode, 0.1 M Bu_4NClO_4).

pivalate fragments from the complex molecule or, at least, can change its coordination mode with the metal center. An analogous peak was found in studying the electrochemical properties of the complexes in a solvent mixture (MeCN—CH_2Cl_2). The second redox processes in the anodic region were observed at rather similar potentials for the hexanuclear compounds and correspond to oxidation of the coordinated terminal pyridone molecules. The potentials of the second anodic peaks for compounds **3** and **4** are slightly shifted in the cathode area compared to the free ligand (1.627 V). The free ligand in DMF is oxidized in the two-electron irreversible process unlike the reaction in CH_2Cl_2, where the process (according to the available data, see Table 2) is one-electron and weakly reversible. The irreversibility of the second oxidation step for compounds **3** and **4** and an insignificant cathodic shift of the potential compared to that of the free ligand are indicative of weak coordination of the neutral pyridone ligands to the metal center.

To estimate the influence of hydroxopyridine derivatives on the electrochemical behavior of polynuclear nickel pivalates, we studied the electrochemical behavior of the starting nonanuclear nickel carboxylate complex **2** containing no anions L. Oxidation of **2** proceeds in one irreversible multielectron step involving, apparently, the metal ions in the redox process (see Table 2).

It is known[25] that the redox reactions of carboxylate complexes of d-metals can formally be divided into three groups: 1) reactions accompanied by a change in the oxidation state of only the metal ion; 2) reactions involving terminal ligands; 3) reactions leading not only to a change in the oxidation state of metal but also to the rearrangement of the inner structure of the complex. Nonanuclear nickel complex **2** can be assigned to the third group. The electrochemical behavior of nonanuclear complex **2** is noticeably different from that of decanuclear complex **5**, in which the partial replacement of the carboxylate fragments by the pyridonate anions leads to a decrease in the oxidation potential of the complex and reversibility of redox transitions. The observed changes in the electrochemical characteristics are indicative of a considerable decrease in the HOMO energy and an increase in the contribution of the pyridonate fragments to HOMO. The formation of stable oxidized forms for complex **5** suggests that complex **5** is characterized by higher electron lability than compound **2**.

The differences in the redox behavior of complexes **5** and **2** are observed also in the cathodic region. Reduction of decanuclear complex **5** is a one-electron weakly reversible process and corresponds to reduction of one metal center (Fig. 7). Reduction of carboxylate complex **2** is a multielectron irreversible process occurring at higher cathodic potentials and resulting in partial destruction of the complex. The reverse scan of the cyclic voltammogram shows a peak at −0.08 V, which is presumably assigned to oxidation of nickel metal adsorbed on the surface of the auxiliary electrode. The cyclic voltammogram of complex **5** provides evidence that there are no decomposition products in this case (see Fig. 7). Reduction is shifted to more positive potentials compared to carboxylate complex **2**. Therefore, based on the electrochemical data for complex **5**, it can be concluded that the frontier redox orbitals approximate each other by ~1 V compared to carboxylate complex **2**.

Reduction of hexanuclear complexes **3** and **4** proceeds identically. The cyclic voltammograms show irreversible one-electron redox transitions at virtually equal potentials (Fig. 8, curve *1*). However, the cyclic voltammogram of compounds **3** has an additional cathodic step at −1.864 V. Upon the replacement of the solvent with CH_2Cl_2 in the case of complex **3**, the results were analogous to those obtained in DMF. The anodic scan of the

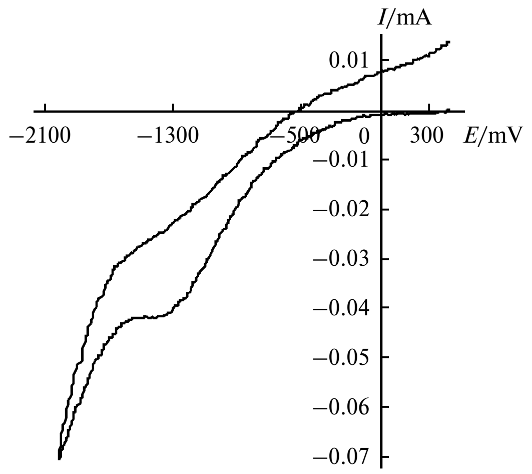


Fig. 7. CV data for reduction of **5** (0—−2000 mV) (CH_2Cl_2, $V = 0.2$ V s^{-1}, Ag/AgCl, $C = 3 \cdot 10^{-3}$ mol L^{-1}, Pt electrode, 0.1 M Bu_4NClO_4).

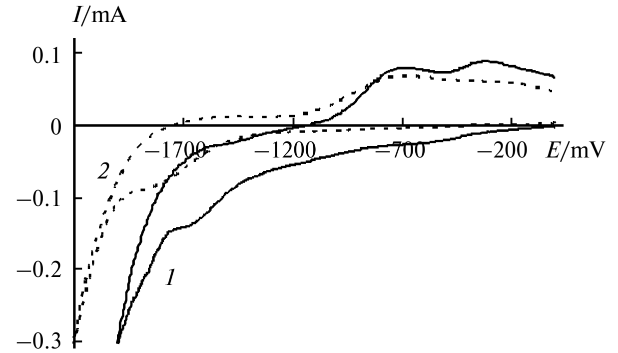


Fig. 8. CV data for reduction: *1*, complex **3**; *2*, 2-hydroxy-6-methylpyridine (**1**) (DMF, $V = 0.2$ V s^{-1}, Ag/AgCl, $C = 3 \cdot 10^{-3}$ mol L^{-1}, Ar, Pt electrode, 0.1 *M* Bu_4NClO_4).

voltammogram is evidence for the presence of products of the chemical reaction proceeding after the electron transfer (−0.727 and −0.400 V). An analysis of the cyclic voltammograms of the coordinated ligand in complexes **3** and **4** revealed the presence of analogous anodic peaks (see Fig. 8, curve *2*).

Consequently, compounds **3** and **4**, unlike decanuclear complex **5**, are characterized by redox activity of the coordinated ligands at cathodic potentials as well. Reduction occurs at the terminal pyridone fragments to give reduction products of the ligand in solution. However, an additional wave is observed in the case of complex **3** at −1.864 V. This wave belongs, apparently, to the ligand-centered process. As in the case of compound **3**, the reverse scan of the cyclic voltammogram of complex **4** shows only oxidation peaks of reduction products of the ligand, whereas the oxidation peak of adsorbed metal is absent. Unlike complex **2**, reduction of complexes **3** and **4** does not lead to degradation of the metal core and release of free metal.

Therefore, the redox activity of the coordinated neutral pyridone ligands and the weak involvement of the inner coordination sphere in redox processes are more typical of complexes **3** and **4**. The replacement of the carboxylate anions by the pyridonate anions and poor steric accessibility of the metal centers lead to a decrease in the efficiency of the system in the internal charge transfer and charge delocalization in the system compared to the decanuclear complex. In the case of decanuclear complex **5**, reversible redox transitions occur as a result of an increase in the number of metal centers, due to which this complex can be considered as an electronic buffer.

Experimental

The complexes were synthesized under argon with the use of dehydrated commercial solvents. 2-Hydroxy-6-methylpyridine was purchased from Acros. The starting nonanuclear nickel pivalate was synthesized according to a known procedure.[26] The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibility χ'_{M} was measured on a Quantum Design MPMS-5S SQUID magnetometer in the temperature range of 300—2 K. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi'_{M}T)^{1/2}$.[27] Electrochemical studies were carried out on a digital IPC-PRO potentiostat/galvanostat equipped with a 2-mL three-electrode electrochemical cell. A platinum electrode with a surface area of 4 mm^2 was used as the working electrode, a platinum plate with a surface area of 70 mm^2 served as the auxiliary electrode, a saturated silver chloride electrode with a water-impermeable membrane was used as the reference electrode, and tetrabutylammonium perchlorate (0.1 mol L^{-1}) served as the supporting electrolyte. The starting concentration of the compounds was 0.003—0.001 mol L^{-1}. The cyclic voltammograms were recorded at a potential scan rate of 0.2 V s^{-1}. The complexes were dissolved and the cyclic voltammograms were recorded under argon.

Bis(μ_3-hydroxo)bis(μ_3-trimethylacetato-*O,O,O′*)hexakis(μ-trimethylacetato-*O,O′*)bis(η-trimethylacetato)bis(μ_2-6-methyl-2-pyridone-*O*)bis(η-6-methyl-2-pyridone)bis(μ_2-aqua)hexanickel(II), $(HL)_2(\mu_2\text{-}HL)_2Ni_6(\mu_3\text{-}OH)_2(\mu_2\text{-}H_2O)_2(\mu\text{-}OOCCMe_3)_8(\eta\text{-}OOCCMe_3)_2$ (3). A solution of 2-hydroxy-6-methylpyridine (0.0837 g, 0.77 mmol) in acetonitrile (10 mL) was added to a solution of the $Ni_9(OH)_6(\mu\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ complex (0.2 g, 0.77 mmol) in acetonitrile (10 mL). The reaction solution was stirred at room temperature for 5 min. After 10—15 min, a finely crystalline precipitate was obtained. Crystals suitable for X-ray diffraction were grown by slow evaporation of the dilute reaction solution at room temperature. The yield of compound **3** was 0.14 g (60% based on consumed nickel). Found (%): C, 47.5; H, 6.7; N, 3.0. $C_{74}H_{124}N_4Ni_6O_{28}$. Calculated (%): C, 47.4; H, 6.6; N, 3.0. IR (KBr), ν/cm^{-1}: 2980 m, 2956 m, 2924 m, 2868 m, 1668 s, 1652 s, 1644 s, 1624 s, 1556 s, 1536 s, 1480 s, 1456 s, 1416 s, 1356 s, 1276 m, 1224 s, 1164 s, 1028 s, 1000 s, 936 m, 916 m, 876 s, 816 m, 788 s, 744 m, 724 m, 608 s, 572 m, 584 m, 548 m, 532 m, 464 w, 424 s.

(μ_3-Hydroxo)tris(μ_3,η^2-6-methyl-2-pyridonato)(μ_2,η^2-6-methyl-2-pyridonato)(μ_3-6-methyl-2-pyridonato)(μ_3-trimethylacetato-*O,O,O′*)tetrakis(μ-trimethylacetato-*O,O′*)(η^2-trimethylacetato-*O,O′*)(η-6-methyl-2-pyridone)hexanickel(II), $(HL)Ni_6(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}L)_3(\mu,\eta^2\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)$ (4). A solution of 2-hydroxy-6-methylpyridine (0.0837 g, 0.77 mmol) in acetonitrile (15 mL) was added to a solution of the $Ni_9(OH)_6(\mu\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ complex (0.2 g, 0.77 mmol) in acetonitrile (15 mL). The reaction solution was heated at 80 °C for 4 h without stirring and then cooled to room temperature on a sand bath. As the solution was cooled, small prismatic crystals precipitated. The yield of compound **4** was 0.11 g (53%). Found (%): C, 48.8; H, 5.6; N, 5.2. $C_{66}H_{91}N_6Ni_6O_{19}$. Calculated (%): C, 48.6; H, 5.6; N, 5.1. IR (KBr), ν/cm^{-1}: 3600—3290 m, 2952 s, 2924 s, 2864 m, 1648 s, 1604 s, 1572 v.s, 1564 v.s, 1480 s, 1468 v.s, 1412 v.s, 1372 s, 1356 s, 1332 s, 1264 w, 1248 s, 1228 s, 1156 m, 1080 w, 1044 s, 1012 m, 956 m, 892 m, 868 m, 796 s, 748 s, 676 m, 612 s, 584 m, 524 m, 460 m, 432 m.

Crystals suitable for X-ray diffraction were grown by slow diffusion of a solution of **1** into a solution of **2** in acetonitrile.

Bis(μ_3-oxo)tetrakis(μ_3-hydroxo)hexakis(μ-trimethylacetato-*O,O′*)hexakis(μ_3,η^2-6-methyl-2-pyridonato)hexa-

Table 3. Crystallographic parameters of complexes **3**, **4**, and **5**

Parameter	**3**	**4**	**5**
Molecular formula	$C_{74}H_{124}N_4Ni_6O_{28}$	$C_{66}H_{91}N_6Ni_6O_{19}$	$C_{78}H_{131}N_6Ni_{10}O_{32}$
Molecular weight	1870.03	1624.71	2251.99
Crystal system	Monoclinic	Monoclinic	Cubic
Space group	*C*2/*c*	*P*2(1)/*c*	*P*2(1)3
a/Å	25.522(7)	19.646(4)	22.591(3)
b/Å	17.587(4)	15.130(3)	22.591(3)
c/Å	19.834(6)	24.851(5)	22.591(3)
α/deg	90.00	90.00	90.00
β/deg	91.535(10)	96.095(7)	90.00
γ/deg	90.00	90.00	90.00
V/Å	8899(4)	7345(2)	11529(2)
Z	4	4	4
ρ_{calc}/g cm^{-3}	1.396	1.469	1.297
μ/cm^{-3}	1.319	1.578	1.660
Radiation	Mo-Kα (λ = 0.71073 Å)		
Scan range, θ_{min}—θ_{max}/deg	1.41—25.16	1.04—30.05	1.80—26.01
Number of measured reflections	14964	70446	3520
Number of reflections with $I > 2\sigma(I)$	7793	21215	3104
R_1[a]	0.0439	0.0504	0.0699
wR_2[b]	0.0654	0.0933	0.0955

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

kis(ethanol-*O*)decanickel(II) dihydrate, $[Ni_{10}(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_4(\mu\text{-}OOCCMe_3)_6(\mu_3,\eta^2\text{-}L)_6(EtOH)_6]\cdot(H_2O)_2$ (5). *A.* Ethanol (20 mL) was added to a mixture of the $Ni_9(OH)_6(\mu\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ complex (0.5 g, 1.92 mmol) and 2-hydroxy-6-methylpyridine (0.2090 g, 1.92 mmol), and the reaction mixture was stirred at 60 °C until the reagents were completely dissolved. Then the solution was kept at room temperature for 24 h. The green crystals that precipitated were separated from the solution by decantation, washed with cold ethanol, and dried at 0.1 Torr (20 °C). The yield of compound **5** was 0.19 g (44%). Calculated (%): C, 41.6; H, 5.9; N, 3.7. $C_{78}H_{131}N_6Ni_{10}O_{32}$. Found (%): C, 41.4; H, 5.7; N, 3.7. IR (KBr), ν/cm^{-1}: 3612 m, 3600—3200 m, 2976 m, 2956 s, 2924 s, 2868 m, 1652 m, 1604 s, 1572 v.s, 1564 v.s, 1480 s, 1468 v.s, 1412 s, 1372 s, 1356 s, 1332 v.s, 1264 m, 1248 s, 1228 s, 1156 s, 1092 m, 1048 s, 1012 m, 956 m, 892 m, 884 m, 872 m, 796 s, 748 s, 676 m, 612 m, 584 w, 524 w, 460 w, 432 m.

X-ray diffraction study. X-ray diffraction data sets for complexes **3**, **4**, and **5** were collected using the standard procedure[28] on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 120 K (for **3** and **4**) and 293 K (for **5**), ω-scanning technique, the scan step was 0.3°, the exposure time per frame was 30 s). For all complexes, a semi-empirical absorption correction was applied.[29] The crystallographic parameters and the X-ray diffraction data collection and refinement statistics for all structures are given in Table 3. The structures were solved by direct methods using the SHELXS97 program package[30] and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms (positions of H atoms were fixed with $U_H = 0.082$) using the SHELXL97 program package.[31] The hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands and NH groups were generated geometrically and refined using a riding model. The calculations were carried out using the SHELX97 program package.[30] Selected geometric parameters of the complexes are given in Table 1.

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