Synthesis, structures, and magnetic properties of binuclear carboxylate complexes with Ni^{II} and Ni^{III} atoms

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The reaction of $NiCl_2 \cdot 6H_2O$ with Me_3CCOOH and KOH taken in a molar ratio of 1 : 2 : 2 in water afforded the nonanuclear antiferromagnetic complex $[Ni_9(Me_3CCOOH)_4(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}]$, which apparently contains Ni^{II} and Ni^{III} atoms. The complex was isolated by extraction with CH_2Cl_2, benzene, or hexane. The reactions of this complex with pyridine bases (pyridine (Py), 3,4-lutidine (Lut), and nicorandil (Nic)) gave the adducts $L_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (L = Py, Lut, or Nic, respectively). According to magnetic measurements, intramolecular ferromagnetic exchange interactions in these adducts are complemented by intermolecular antiferromagnetic interactions. Pyrolysis of the pyridine adduct in air or under an inert atmosphere in xylene yielded the antiferromagnetic complex $Py_2Ni_2(Me_3CCOOH)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$, which contains Ni^{II} atoms. The structures of all the complexes synthesized were established by X-ray diffraction analysis. The electronic absorption spectra of these compounds are considered.

Key words: nickel clusters, mixed-valence complexes, carboxylate ligands, X-ray diffraction analysis, magnetic properties, UV and IR spectra.

Recently, we have demonstrated that cardioactive nicorandil, *N*-(2-nitroxyethyl)nicotinamide (Nic), reacts readily with copper and platinum halides owing to the pyridine moiety of the molecule to form 2 : 1 adducts of the general formula Nic_2MX_2 (M = Cu and X = Br;[1] M = Pt and X = Cl [2]). The reactions of nicorandil with Cu^{II} and Rh^{II} binuclear tetracarboxylates afforded the $Nic_2M_2(OOCCMe_3)_4$ adducts.[1] The platinum and rhodium compounds synthesized exhibit high antimetastatic activity, which gave impetus to a further search for new bioactive compounds of this type that would contain more accessible 3d elements. Binuclear nickel tetracarboxylates with axial N-donor ligands have been reported previously.[3,4] They were synthesized by reactions of $NiCl_2 \cdot 6H_2O$ with potassium (or sodium) pivalate followed by treatment of the reaction mixture with α-substituted pyridine bases. However, the dimers were obtained in low yields. The major reaction product was a blue complex, which, in the authors' opinion,[3,4] had a monomeric structure. Both monomeric and dimeric nickel complexes that contain the bound nicorandil molecule are of interest with respect to their potential antitumor activity. Therefore, in this work we studied the possibilities of the synthesis of these compounds.

Results and Discussion

Treatment of $NiCl_2 \cdot 6H_2O$ with pivalic acid and KOH (the ratio of the reagents was varied from 1 : 2 : 2 to 1 : 4 : 4) in water followed by extraction of the product with CH_2Cl_2, benzene, or hexane afforded pale-green prismatic crystals of a complex that contains (according to the data of elemental analysis) 1.80 carboxylate groups (in the protonated or deprotonated form) and ~0.65 oxygen atoms (as oxo, hydroxo, or aqua groups) per nickel atom. The reaction with the use of potassium pivalate, which has been prepared preliminarily, gave a complex of analogous composition. The structure of this compound has not been studied previously (after treatment of the reaction mixture with pyridine bases, only binuclear tetracarboxylates were isolated[3,4]). Therefore,

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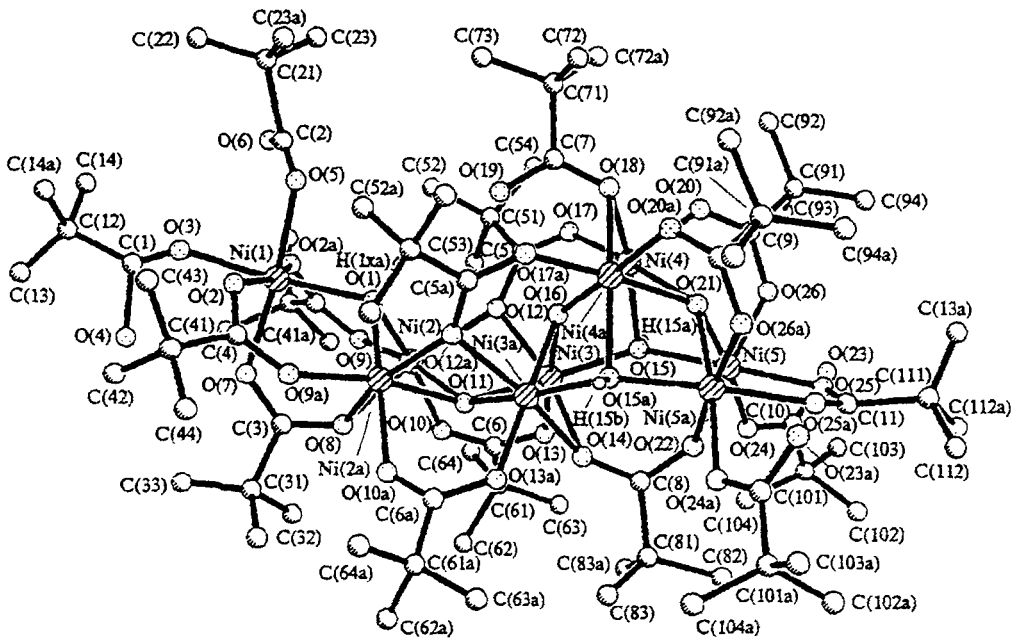

Fig. 1. Structure of nonanuclear cluster **1** (only the H atoms of the suggested μ_3-OH groups, which were generated geometrically, are shown).

we studied very unstable crystals of **1** by X-ray diffraction analysis. It was found that complex **1** is a nonanuclear cluster (Fig. 1, Tables 1 and 2) in which four pairs of nickel atoms (the Ni...Ni distances in the pairs are nonequivalent: Ni(2)...Ni(2a), 2.826(2) Å; Ni(3)—Ni(3a), 2.746(2) Å; Ni(4)—Ni(4a), 2.724(2) Å; Ni(5)—Ni(5a), 3.056(2) Å) are arranged as a bent ribbon (the distances between the adjacent nickel atoms in different pairs are in the range of 2.916(2)—2.924(2) Å). The ninth nickel atom is bonded to the metal atoms of the last pair (Ni(1)...Ni(2) or Ni(2a), 3.383(2) Å) through the tridentate oxygen atom (Ni(1)—O(1), 2.045(8) Å; Ni(2)—O(1), 2.047(6) Å) and three bridging carboxylate groups (Ni—O, 1.997(6)—2.146(6) Å) and bears two terminal-coordinated carboxylate groups (Ni(1)—O, 2.031(11) and 2.113(11) Å). Each two pairs of the nickel atoms form a rectangle, whose center is occupied by the O atom, which deviates slightly from the Ni_4 plane (by 0.515, 0.511, and 0.656 Å from the Ni(2)Ni(2a)Ni(3)Ni(3a), Ni(3)Ni(3a)Ni(4)Ni(4a), and Ni(4)Ni(4a)Ni(5)Ni(5a) planes, respectively). Judging from the geometric characteristics of these fragments, the O atoms belong more likely to the μ_4-oxo groups than to the hydroxo groups and even less probably to the aqua ligands. At the same time, the above-mentioned μ_3-O atom, which is located in the center of the terminal Ni_3 fragment formed by the Ni(1), Ni(2), and Ni(2a) atoms, belongs, apparently, either to a hydroxo or to an aqua group and deviates by 0.849 Å from the plane formed by the metal atoms, like two other analogous μ_3-O groups in the M_3 triangles, which are formed by the metal atoms

Table 1. Bond lengths (*d*) in cluster **1**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)—O(1)	2.045(8)	Ni(5)—O(22)	2.125(6)
Ni(1)—O(2)	2.023(6)	Ni(5)—O(24)	2.112(7)
Ni(1)—O(3)	2.113(11)	Ni(5)—O(25)	1.997(7)
Ni(1)—O(5)	2.031(11)	Ni(5)—O(26)	2.062(7)
Ni(1)—O(7)	2.069(9)	O(2)—C(4)	1.262(11)
Ni(2)—O(1)	2.047(6)	O(3)—C(1)	1.031(29)
Ni(2)—O(8)	2.148(6)	O(4)—C(1)	1.545(29)
Ni(2)—O(9)	1.997(6)	O(5)—C(2)	0.981(24)
Ni(2)—O(10)	2.009(6)	O(6)—C(2)	1.365(21)
Ni(2)—O(11)	2.121(6)	O(7)—C(3)	1.267(16)
Ni(2)—O(12)	2.162(6)	O(8)—C(3)	1.279(16)
Ni(3)—O(11)	2.115(6)	O(10)—C(6)	1.243(11)
Ni(3)—O(12)	2.066(6)	O(12)—C(5)	1.311(11)
Ni(3)—O(13)	1.983(6)	O(13)—C(6)	1.284(11)
Ni(3)—O(14)	2.150(7)	O(14)—C(8)	1.273(17)
Ni(3)—O(15)	2.015(6)	O(17)—C(5)	1.230(11)
Ni(3)—O(16)	2.052(6)	O(18)—C(7)	1.262(17)
Ni(4)—O(15)	2.035(6)	O(19)—C(7)	1.303(18)
Ni(4)—O(16)	2.081(6)	O(20)—C(9)	1.228(13)
Ni(4)—O(17)	2.003(6)	O(22)—C(8)	1.285(16)
Ni(4)—O(18)	2.109(7)	O(23)—C(10)	1.323(14)
Ni(4)—O(20)	1.989(6)	O(24)—C(10)	1.249(13)
Ni(4)—O(21)	2.165(7)	O(25)—C(11)	1.237(11)
Ni(5)—O(15)	2.023(6)	O(26)—C(9)	1.290(14)
Ni(5)—O(21)	2.149(6)		

from the three first sequentially located pairs (0.735 Å for the Ni(3)Ni(4)Ni(5) and Ni(3a)Ni(4a)Ni(5a) planes). In contrast, the tridentate O atom in the known trinuclear μ_3-oxo complexes of transition metals is located in the M_3 plane (for R = CMe_3, see, for example, Refs. 5—8).

Unfortunately, H atoms in this structure could not be located from the electron density synthesis, which made the determination of the exact composition of the complex and the spin state of the metal atoms substantially more difficult. However, it should be noted that all the four terminal carboxylate groups (in addition to the two above-mentioned groups, there are two groups bonded to the Ni atoms of the first pair) are apparently protonated, which results in the inequality of the C—O distances (see Table 1). Thus, the composition of complex **1** can be described as $Ni_9(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(HOOCCMe_3)_4(OOCCMe_3)_{12}$ or $Ni_9(\mu_4\text{-}O)_3(\mu_3\text{-}OH_2)_3(HOOCCMe_3)_4(OOCCMe_3)_{12}$. In the former case, the molecule contains six Ni^{II} atoms and three Ni^{III} atoms, while in the latter case, the molecule contains only Ni^{II} atoms.

Magnetic measurements for compound **1** in the 296—83 K range demonstrated that the effective magnetic moment per metal atom decreases from 2.58 to 1.99 μB. The data obtained do not allow us to favor one of the two suggested formulas because of substantial spin-spin antiferromagnetic interactions. The spin states of the metal atoms and, correspondingly, the exchange parameters cannot be determined because of the complicated structure of the complex and the lack of an adequate model for calculations.

The IR spectra of complex **1** have stretching vibration bands of the bridging carboxylate groups (ν_s = 1573 and 1610 cm^{-1}; ν_{as} = 1369 and 1425 cm^{-1}), the OCO frag-

Table 2. Bond angles (ω) in cluster **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—Ni(1)—O(2)	98.0(2)	Ni(2)—O(8)—Ni(2a)	82.2(3)	O(12)—Ni(3)—O(16)	88.5(3)
O(2)—Ni(1)—O(3)	81.9(2)	Ni(2)—O(11)—Ni(2a)	83.5(3)	O(14)—Ni(3)—O(16)	86.8(3)
O(2)—Ni(1)—O(5)	88.6(2)	Ni(2)—O(11)—Ni(3a)	151.8(4)	O(15)—Ni(4)—O(16)	83.2(3)
O(1)—Ni(1)—O(7)	96.7(3)	Ni(2a)—O(11)—Ni(3a)	91.0(1)	O(16)—Ni(4)—O(17)	94.3(2)
O(3)—Ni(1)—O(7)	86.7(4)	Ni(3)—O(14)—Ni(3a)	79.4(3)	O(16)—Ni(4)—O(18)	81.2(3)
O(1)—Ni(1)—O(2a)	98.0(2)	Ni(3)—O(15)—Ni(5)	132.0(3)	O(15)—Ni(4)—O(20)	101.9(3)
O(3)—Ni(1)—O(2a)	81.9(2)	Ni(3)—O(16)—Ni(4)	90.1(1)	O(17)—Ni(4)—O(20)	90.1(3)
O(7)—Ni(1)—O(2a)	90.5(2)	Ni(4)—O(16)—Ni(3a)	151.3(4)	O(15)—Ni(4)—O(21)	85.9(3)
O(1)—Ni(2)—O(9)	101.4(3)	Ni(4)—O(16)—Ni(4a)	81.8(3)	O(17)—Ni(4)—O(21)	176.1(3)
O(1)—Ni(2)—O(10)	169.1(2)	Ni(4)—O(18)—Ni(4a)	80.5(3)	O(20)—Ni(4)—O(21)	92.6(3)
O(9)—Ni(2)—O(10)	84.2(2)	Ni(4)—O(21)—Ni(4a)	78.0(3)	O(15)—Ni(5)—O(22)	94.8(3)
O(8)—Ni(2)—O(11)	76.1(3)	Ni(4)—O(21)—Ni(5a)	143.9(4)	O(15)—Ni(5)—O(24)	89.3(2)
O(10)—Ni(2)—O(11)	88.7(3)	Ni(4a)—O(21)—Ni(5a)	85.0(1)	O(22)—Ni(5)—O(24)	94.1(3)
O(8)—Ni(2)—O(12)	159.1(2)	C(8)—O(22)—Ni(5a)	124.7(5)	O(21)—Ni(5)—O(25)	99.0(3)
O(10)—Ni(2)—O(12)	90.3(2)	O(5)—C(2)—O(6)	128.6(21)	O(24)—Ni(5)—O(25)	85.2(3)
O(11)—Ni(3)—O(12)	85.8(3)	O(2)—C(4)—O(9a)	123.8(8)	O(21)—Ni(5)—O(26)	94.4(3)
O(12)—Ni(3)—O(13)	91.2(2)	O(10)—C(6)—O(13)	125.0(8)	O(24)—Ni(5)—O(26)	89.2(3)
O(12)—Ni(3)—O(14)	163.4(2)	O(14)—C(8)—O(22)	123.5(13)	Ni(1)—O(1)—Ni(2)	111.6(3)
O(11)—Ni(3)—O(15)	162.7(2)	O(23)—C(10)—O(24)	121.8(10)	Ni(2)—O(1)—Ni(2a)	87.3(3)
O(13)—Ni(3)—O(15)	93.9(2)	O(1)—Ni(1)—O(3)	176.6(4)	Ni(2)—O(11)—Ni(3)	91.0(1)
O(11)—Ni(3)—O(16)	80.9(3)	O(1)—Ni(1)—O(5)	89.8(4)	Ni(3)—O(11)—Ni(2a)	151.8(4)
O(13)—Ni(3)—O(16)	178.1(2)	O(3)—Ni(1)—O(5)	86.7(4)	Ni(3)—O(11)—Ni(3a)	81.0(3)
O(15)—Ni(3)—O(16)	84.4(3)	O(2)—Ni(1)—O(7)	90.5(2)	Ni(2)—O(12)—Ni(3)	91.2(2)
O(15)—Ni(4)—O(17)	90.7(2)	O(5)—Ni(1)—O(7)	173.5(4)	Ni(3)—O(15)—Ni(4)	92.4(2)
O(15)—Ni(4)—O(18)	162.6(2)	O(2)—Ni(1)—O(2a)	163.7(4)	Ni(4)—O(15)—Ni(5)	91.9(2)
O(17)—Ni(4)—O(18)	98.0(3)	O(5)—Ni(1)—O(2a)	88.6(2)	Ni(3)—O(16)—Ni(3a)	84.0(3)
O(16)—Ni(4)—O(20)	173.3(2)	O(1)—Ni(2)—O(8)	78.1(3)	Ni(3)—O(16)—Ni(4a)	151.3(4)
O(18)—Ni(4)—O(20)	93.2(3)	O(8)—Ni(2)—O(9)	96.6(2)	Ni(3a)—O(16)—Ni(4a)	90.1(1)
O(16)—Ni(4)—O(21)	83.4(3)	O(8)—Ni(2)—O(10)	92.0(3)	Ni(4)—O(21)—Ni(5)	85.0(1)
O(18)—Ni(4)—O(21)	84.7(3)	O(1)—Ni(2)—O(11)	84.5(3)	Ni(5)—O(21)—Ni(4a)	143.9(4)
O(15)—Ni(5)—O(21)	86.7(3)	O(9)—Ni(2)—O(11)	169.6(3)	Ni(5)—O(21)—Ni(5a)	90.6(3)
O(21)—Ni(5)—O(22)	82.8(3)	O(1)—Ni(2)—O(12)	97.4(3)	Ni(5)—O(22)—Ni(5a)	92.0(3)
O(21)—Ni(5)—O(24)	174.7(3)	O(9)—Ni(2)—O(12)	104.2(2)	O(3)—C(1)—O(4)	112.1(19)
O(15)—Ni(5)—O(25)	173.7(3)	O(11)—Ni(2)—O(12)	83.2(2)	O(7)—C(3)—O(8)	123.8(12)
O(22)—Ni(5)—O(25)	88.8(3)	O(11)—Ni(3)—O(13)	100.9(3)	O(12)—C(5)—O(17)	123.7(8)
O(15)—Ni(5)—O(26)	90.8(3)	O(11)—Ni(3)—O(14)	77.7(3)	O(18)—C(7)—O(19)	125.0(13)
O(22)—Ni(5)—O(26)	173.6(3)	O(13)—Ni(3)—O(14)	94.1(2)	O(20)—C(9)—O(26)	123.7(9)
O(25)—Ni(5)—O(26)	86.0(3)	O(12)—Ni(3)—O(15)	103.1(2)	O(25)—C(11)—O(25a)	126.1(16)
Ni(1)—O(1)—Ni(2a)	111.6(3)	O(14)—Ni(3)—O(15)	92.3(3)		

Table 3. Absorption spectra ($\nu \cdot 10^{-3}$ /cm^{-1} (ε/L mol^{-1} cm^{-1})) and diffuse reflection spectra [$\nu \cdot 10^{-3}$ /cm^{-1}] of complexes **1**—**4** and **6**

Compound	UV region, Charge transfer bands		Visible region, Ligand field transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^1E_g(^1D)$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	Near IR region
1	[>44.5]		[25.0]	[14.28]; [12.82] sh	[8.69]; [8.10] sh;	[5.93]; [5.41];
		31.46 sh (14)	25.0 (33)	14.64 (12); 13.68 sh (9)	[7.41] sh	[5.0]; [4.41]
2	[38.31];	[33.22]	[26.38]	[15.80]; [13.32]	[9.38]	[6.00]; [5.90]
3	[38.31];	[33.22]	[26.38]	[15.95]; [13.23]	[9.43]	[5.88]; [5.71]
4	[37.45];	[30.96]	[22.37]	[15.80]; [13.32]	[9.53]	[6.00]; [5.88]
		32.0 sh (22)	25.84 (45)	15.44 (16); 13.68 (10)		
7	[37.04];	[30.30]	[25.0]	[14.93]; [11.11]	[8.93]; [7.58]; [7.35] sh	[6.33] sh; [5.65]; [5.03]; [4.54]
$Ni(H_2O)_6^{2+}$ *			[25.30]	[15.20]; [13.80]	[8.50]	
$Ni(acac)_2Py_2$*				[17.39]	[10.15]	
$NiPy_6^{2+}$ *			[27.0]	[16.50]	[10.15]	

* See Ref. 9.

ments of the terminal-coordinated pivalic acid (ν(OCO) = 1703 cm^{-1}), and the OH groups (3457 cm^{-1}).

In the visible region of the absorption spectrum of a solution of cluster **1** in THF, three bands with maxima at ν = 8690, 14280, and 25000 cm^{-1} are observed. These bands correspond to spin-allowed ligand field transitions of the octahedral $[Ni^{II}O_6]$ chromophore. An analogous situation was observed in the case of the $Ni(H_2O)_6^{2+}$ ion.[9,10] In cluster **1**, the long-wave branch of the second band of the absorption spectrum has a shoulder at 12820 cm^{-1}, as in the case of a nickel hexaaqua dication. Thus, the splitting parameter 10Dq = 8690 cm^{-1} calculated for compound **1** agrees well with that of the above-mentioned dication (8500 cm^{-1}).

The UV spectrum of a solution of **1** shows only an ascending branch of an intense charge transfer band, whose maximum is above 45000 cm^{-1}. In the low-energy region of this branch, a shoulder occurs at 31640 cm^{-1}.

It should be noted that the absorption spectrum of a solution of cluster **1** virtually coincides with the diffuse reflection spectrum of a polycrystal sample of **1** at room temperature (Table 3, Fig. 2) in the region of ligand field transitions due, apparently, to retention of the molecular structure upon dissolution in THF. However, in the region of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition of the diffuse reflection spectrum of compound **1**, two additional components are well resolved as shoulders at 8100 and 7410 cm^{-1}, whereas in the 6700—4300 cm^{-1} region, a series of weak bands is observed. If the effective symmetry of the environment about the Ni atoms in the structure of cluster **1** is lower than O_h, these bands can be determined, for example, by vibrational overtones of the stretching bands of the OH groups of the molecule. In spite of the detailed spectroscopic study of compound **1**, we failed to unambiguously answer the question of whether Ni^{III} atoms are present in the molecule, because ligand field transitions for both ions, Ni^{II} and Ni^{III}, can have close energy positions.[11,12] Thus according to the published data,[11] the spectrum of Ni^{III} in the lattice of corundum (Al_2O_3) consists of several narrow low-intensity bands at about 13300 cm^{-1}, two broad

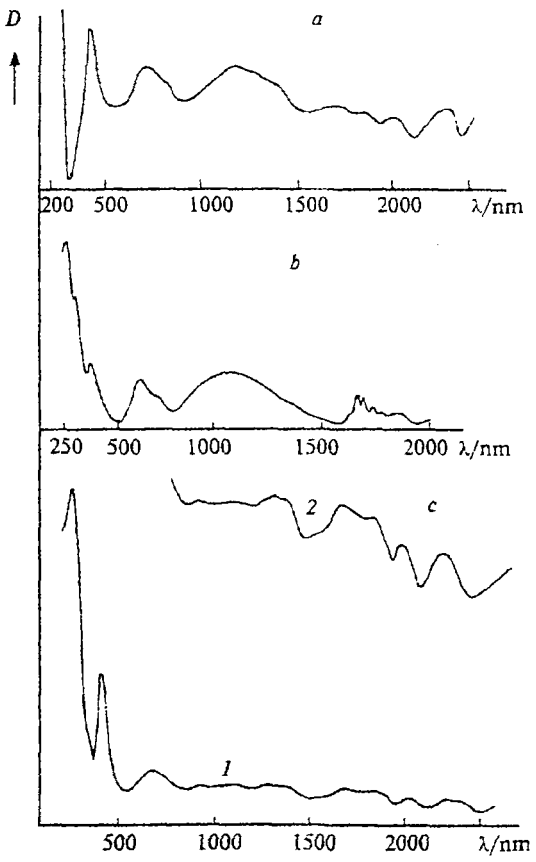

Fig. 2. Diffuse reflection spectra of polycrystalline samples of compounds **1** (*a*), **2** (*b*), and **7** (*c*) and the electronic spectrum of a solution of compound **7** in THF (*d*).

bands at about 16300—16800 cm^{-1} and 17800—19900 cm^{-1}, and a series of rather intense bands in the near UV region, which belong to charge transfer transitions. In addition, the equally probable low-spin $(t_{2g})^6e_g^1$ and high-spin $(t_{2g})^5e_g^2$ configurations of the Ni^{III} ion with close energies can result in mixing of their ligand field transitions, and the ligand field transitions cannot be unambiguously identified even in the low-temperature spectra of single crystals of Cs_2NaNiF_6 (hexagonal unit cell)[12] for which the positions occupied by the low-spin and high-spin Ni^{III} ions have been determined by X-ray diffraction analysis.

Cluster **1** reacts readily with various pyridine bases (including nicorandil) to form blue crystals of the adducts $L_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (L = Py (pyridine) (**2**), Lut (3,4-lutidine) (**3**), or Nic (nicorandil) (**4**)) (Scheme 1). According to the data of X-ray diffraction analysis (Figs. 3—5, Tables 4—9), all the complexes in question have similar geometric characteristics of the binuclear metal fragments. Thus, the metal atoms in the molecules are located at nonbonded distances (Ni...Ni, 3.513(1) Å (**2**), 3.549(3) Å (**3**), and 3.505(4) Å (**4**)). The ligand environments about the metal centers are approximately octahedral. Each Ni atom is bonded to the terminal deprotonated carboxylate group (C—O, 1.237(4)—1.250(3) Å (**2**), 1.22(2)—1.26(2) Å (**3**), and 1.23(2)—1.27(2) Å (**4**); Ni—O, 2.056(2) Å (**2**), 2.099(9) Å (**3**), and 2.02(1)—2.06(1) Å (**4**)), to the two pyridine fragments (Ni—N, 2.104(3)—2.123(4) Å (**2**), 2.09(1)—2.103(9) Å (**3**), and 2.12(1)—2.15(1) Å (**4**)), to the O atoms of the bridging pivalate groups (Ni—O, 2.012(2)—2.037(2) Å (**2**), 1.989(8)—2.023(9) Å (**3**), and 2.00(1)—2.03(1) Å (**4**)), and to the O atom of the bridging hydroxyl fragment (Ni—O, 2.074(2)—2.078(3) Å, the Ni—O—Ni angle is 115.6(1)° (**2**); Ni—O, 2.104(6) Å, the Ni—O—Ni angle is 114.9(2)° (**3**); and Ni—O, 2.07(1)—2.09(1) Å, the Ni—O—Ni angle is 114.4(5)° (**4**)). In the complexes in question, the Ni—O distances and, in particular, the Ni—N distances are substantially elongated compared, for example, to the analogous values in the known antiferromagnetic dimers $L_2Ni_2(OOCR)_4$[13—15] (R = CMe_3, L = 2-methylquinoline,[13] 2,4-lutidine,[14] 2,5-lutidine, 2-ethylpyridine, or 2-picoline;[15] Ni—N, 2.034—2.041 Å), which is typical of electron-excessive complexes. However, the above-mentioned values are close to the corresponding values observed in the complexes $L_4Ni_2(OOCR)_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)$[16,17] (L = Py, R = $2\text{-}ClC_6H_4OCH_2$, Ni—N, 2.104—2.113 Å; L_2 = *N,N,N′,N′*-tetramethylethylenediamine, R = CF_3, Ni—N, 2.131—2.182 Å) and $L_2Ni_2(\mu\text{-}OOCR)_2(\mu\text{-}OH)^+$ (**5**)[18] (L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane, R = Me, Ni—N, 2.136—2.169 Å) with Ni^{II} atoms that have a three-bridged metal framework. Based on the data of thermomagnetic measurements of single-crystal samples (Table 10), it may be concluded that molecules **2**—**4** contain Ni^{II} and Ni^{III} atoms with the formally 18- and 19-electron environments. It should be taken into account that the so-called double exchange effect can be observed in compounds that contain paramagnetic ions of one metal in different oxidation states, which results in the ferromagnetism of the complexes.[19,20] Actually, the effective magnetic moments (per nickel atom) of complexes **2**—**4** depend only slightly on the temperature (2.66 (300 K)—2.61 (5 K) μB for complex **2**, 2.50 (300 K)—2.52 (10 K) μB for complex **3**, and 2.31 (300 K)—2.68 (10 K) μB for complex **4**). This behavior is described by a binuclear model (S_1 = 1, S_2 = 1/2) with intramolecular antiferromagnetic ($2J_{(g)}$ = 17 (**2**), 12 (**3**), and 9 (**4**) cm^{-1}) and weak intermolecular antiferromagnetic ($-2J_m$ = 2.3 (**2**), 4.8 (**3**), and 2 (**4**) cm^{-1}) exchange. Formally, analogous properties have been observed previously for Ni^{II} compounds that con-

Scheme 1

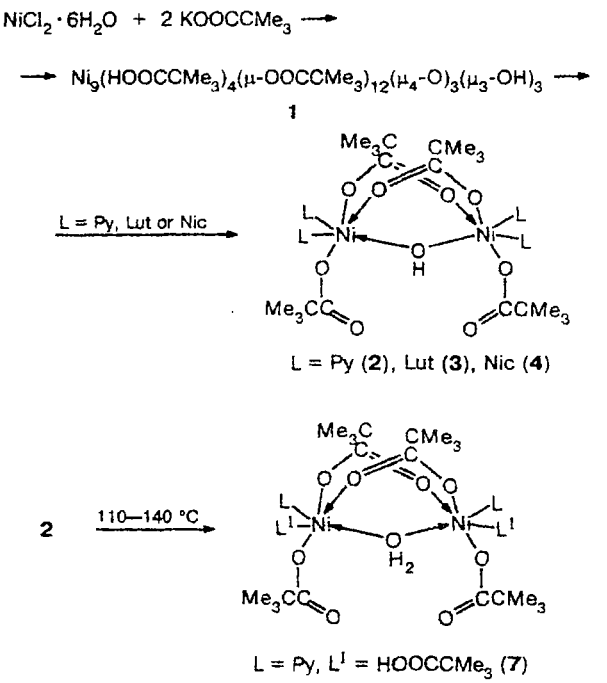

Table 4 Bond lengths (*d*) in complex **2**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)—O(1)	2.037(2)	Ni(2)—N(4)	2.116(3)
Ni(1)—O(3)	2.021(3)	O(1)—C(1)	1.240(5)
Ni(1)—O(5)	2.056(3)	O(2)—C(1)	1.247(4)
Ni(1)—O(9)	2.078(3)	O(3)—C(6)	1.251(5)
Ni(1)—N(1)	2.123(4)	O(4)—C(6)	1.235(5)
Ni(1)—N(2)	2.113(3)	O(5)—C(11)	1.250(6)
Ni(2)—O(2)	2.012(2)	O(6)—C(11)	1.243(5)
Ni(2)—O(4)	2.023(3)	O(7)—C(16)	1.245(4)
Ni(2)—O(7)	2.056(2)	O(8)—C(16)	1.237(5)
Ni(2)—O(9)	2.074(2)	O(9)—H(1)	0.834(7)
Ni(2)—N(3)	2.104(3)		

Table 5. Bond angles (ω) in complex **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—Ni(1)—O(3)	90.8(1)	O(4)—Ni(2)—N(3)	86.4(1)	O(3)—Ni(1)—N(2)	89.7(1)
O(3)—Ni(1)—O(5)	175.7(1)	O(9)—Ni(2)—N(3)	178.4(1)	O(9)—Ni(1)—N(2)	89.1(1)
O(3)—Ni(1)—O(9)	93.8(1)	O(4)—Ni(2)—N(4)	176.5(1)	O(2)—Ni(2)—O(4)	93.0(1)
O(1)—Ni(1)—N(1)	87.6(1)	O(9)—Ni(2)—N(4)	90.9(1)	O(4)—Ni(2)—O(7)	87.6(1)
O(5)—Ni(1)—N(1)	86.7(1)	Ni(1)—O(9)—Ni(2)	115.6(1)	O(4)—Ni(2)—O(9)	92.2(1)
O(1)—Ni(1)—N(2)	177.1(1)	Ni(2)—O(9)—H(1)	115.1(8)	O(2)—Ni(2)—N(3)	87.6(1)
O(5)—Ni(1)—N(2)	91.5(1)	O(1)—Ni(1)—O(5)	87.8(1)	O(7)—Ni(2)—N(3)	88.4(1)
N(1)—Ni(1)—N(2)	89.6(1)	O(1)—Ni(1)—O(9)	93.8(1)	O(2)—Ni(2)—N(4)	88.4(1)
O(2)—Ni(2)—O(7)	175.9(1)	O(5)—Ni(1)—O(9)	90.3(1)	O(7)—Ni(2)—N(4)	90.8(1)
O(2)—Ni(2)—O(9)	91.6(1)	O(3)—Ni(1)—N(1)	89.2(1)	N(3)—Ni(2)—N(4)	90.4(1)
O(7)—Ni(2)—O(9)	92.4(1)	O(9)—Ni(1)—N(1)	176.7(1)	Ni(1)—O(9)—H(1)	129.3(8)

tain three-bridged fragments $Ni(\mu\text{-}OH_2)(\mu\text{-}OOCR)_2$ (L = *N,N,N′,N′*-tetramethylethylenediamine (**6**), R = Me, $ClCH_2$, or Cl_2CH [21]) or $Ni(\mu\text{-}OR)(\mu\text{-}OOCR)_2^+$ with complex polydentate ligands.[22] However, in these cases the effective magnetic moments (3.1—3.4 μB and 3.3—3.6 μB, respectively) are substantially larger and correspond to $S_1 = S_2 = 1$. Our attempt to calculate the exchange parameters with the use of similar spin values unambiguously demonstrated that the model is inadequate. Note that in the IR spectra of this series of complexes, stretching bands of the protonated OCO groups at ~1700 cm^{-1} are not observed. The absorption spectra of complexes **2**—**4** in the region of the ligand field transitions correspond to the NiO_4N_2 chromophore (see Table 3). The spin-allowed bands are shifted hypsochromically (1300—1500 cm^{-1}) compared to their positions in the spectrum of cluster **1**, which contains the NiO_6 chromophore. In addition, these data agree well with the values determined previously for compounds **5** (9800, 15600, and 26600 cm^{-1})[18] and **6** (9100,

Table 6. Bond lengths (*d*) in complex **3**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)—O(1)	2.099(9)	O(2)—C(1)	1.223(18)
Ni(1)—O(3)	2.104(6)	O(3)—Ni(1a)	2.104(6)
Ni(1)—O(4)	1.989(8)	O(4)—C(6)	1.296(18)
Ni(1)—O(5)	2.023(9)	O(5)—C(6a)	1.282(20)
Ni(1)—N(1)	2.088(12)	C(6)—O(5a)	1.282(20)
Ni(1)—N(2)	2.103(9)	O(3)—H(3xa)	0.917(56)
O(1)—C(1)	1.261(16)		

Table 7. Bond angles (ω) in complex **3**

Angle	ω/deg	Angle	ω/deg
O(1)—Ni(1)—O(3)	90.4(3)	O(1)—Ni(1)—O(4)	85.7(3)
O(3)—Ni(1)—O(4)	91.5(3)	O(1)—Ni(1)—O(5)	174.8(4)
O(3)—Ni(1)—O(5)	93.1(3)	O(4)—Ni(1)—O(5)	98.1(3)
O(1)—Ni(1)—N(1)	87.8(4)	O(3)—Ni(1)—N(1)	176.8(3)
O(4)—Ni(1)—N(1)	85.7(4)	O(5)—Ni(1)—N(1)	88.9(4)
O(1)—Ni(1)—N(2)	88.4(4)	O(3)—Ni(1)—N(2)	93.5(3)
O(4)—Ni(1)—N(2)	172.3(4)	O(5)—Ni(1)—N(2)	87.5(4)
N(1)—Ni(1)—N(2)	89.1(4)	Ni(1)—O(3)—Ni(1a)	114.9(5)

Table 8. Bond lengths (*d*) in complex **4**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)—O(1)	2.091(11)	Ni(2)—N(7)	2.125(15)
Ni(1)—O(2)	1.999(12)	Ni(2)—N(10)	2.144(12)
Ni(1)—O(4)	2.030(11)	O(2)—C(6)	1.230(23)
Ni(1)—O(6)	2.018(12)	O(3)—C(6)	1.265(18)
Ni(1)—N(1)	2.131(15)	O(4)—C(1)	1.270(18)
Ni(1)—N(4)	2.155(13)	O(5)—C(1)	1.269(21)
Ni(2)—O(1)	2.077(12)	O(6)—C(11)	1.235(17)
Ni(2)—O(3)	2.019(10)	O(7)—C(11)	1.256(23)
Ni(2)—O(5)	2.024(12)	O(8)—C(16)	1.231(19)
Ni(2)—O(8)	2.062(13)		

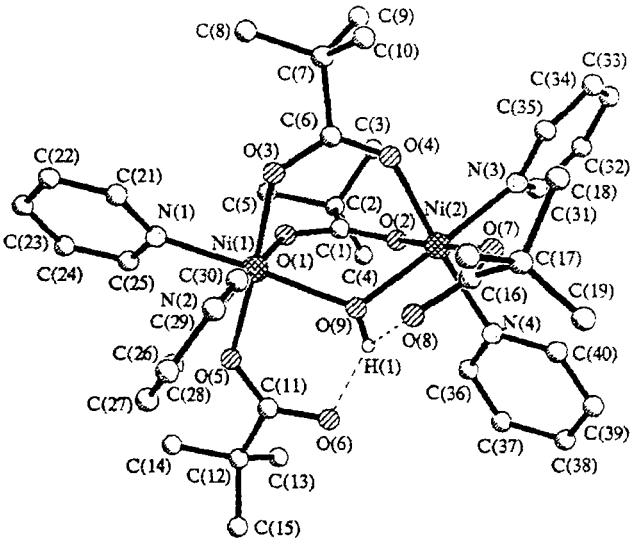

Fig. 3. Structure of the complex $Py_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (**2**).

15450, and 25900 cm^{-1}).[21] In the UV regions of the spectra of dimers **2**—**4**, a complex intense band is observed at ν = 37000—38000 cm^{-1}, which corresponds to the charge transfer band. As in the case of compound **1**, the near IR region (6500—4000 cm^{-1}) of the spectra of complexes **2**—**4** has a number of bands, whose intensities are substantially lower than those in the IR spectrum of compound **1**. The IR spectrum of compound **2** measured as KBr pellets in the 7000—2000 cm^{-1} region (Fig. 6) demonstrated that the bands in the near IR region of the spectra of compounds **2**—**4** occur owing to overtones of the stretching bands of the OH groups.

On storage, heterovalent binuclear complexes **2**—**4** are not soluble any longer in organic solvents, although the spectral characteristics (IR and UV spectra) and the color of the crystals are retained. Heating of adduct **2** in xylene (110—140 °C) for 2—4 h afforded the $Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ complex (**7**), which was isolated as green crystals. Accoridng to the data of X-ray diffraction analysis

Table 9. Bond angles (ω) in complex **4**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—Ni(1)—O(2)	91.2(5)	O(3)—Ni(2)—N(7)	87.1(5)	O(6)—Ni(1)—N(4)	90.9(5)
O(2)—Ni(1)—O(4)	89.5(5)	O(8)—Ni(2)—N(7)	86.7(5)	O(1)—Ni(2)—O(3)	91.4(5)
O(2)—Ni(1)—O(6)	177.1(5)	O(3)—Ni(2)—N(10)	174.6(6)	O(3)—Ni(2)—O(5)	94.8(5)
O(1)—Ni(1)—N(1)	179.7(5)	O(8)—Ni(2)—N(10)	87.8(5)	O(3)—Ni(2)—O(8)	88.1(5)
O(4)—Ni(1)—N(1)	83.5(5)	Ni(1)—O(1)—Ni(2)	114.4(5)	O(1)—Ni(2)—N(7)	177.6(4)
O(1)—Ni(1)—N(4)	91.4(5)	O(1)—Ni(1)—O(4)	96.6(4)	O(5)—Ni(2)—N(7)	87.7(5)
O(4)—Ni(1)—N(4)	172.1(5)	O(1)—Ni(1)—O(6)	91.6(5)	O(1)—Ni(2)—N(10)	92.2(5)
N(1)—Ni(1)—N(4)	88.5(5)	O(4)—Ni(1)—O(6)	89.5(5)	O(5)—Ni(2)—N(10)	88.9(5)
O(1)—Ni(2)—O(5)	94.3(5)	O(2)—Ni(1)—N(1)	88.6(5)	N(7)—Ni(2)—N(10)	89.2(5)
O(1)—Ni(2)—O(8)	91.5(5)	O(6)—Ni(1)—N(1)	88.6(5)		
O(5)—Ni(2)—O(8)	173.5(5)	O(2)—Ni(1)—N(4)	89.8(5)		

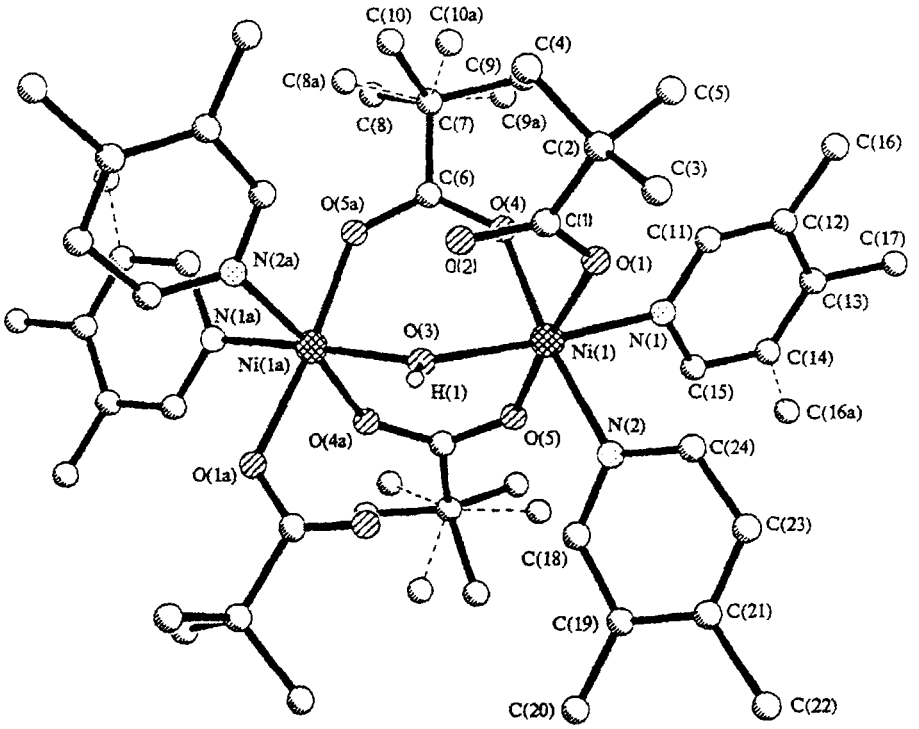

Fig. 4. Structure of the complex $Lut_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (**3**).

Table 10. Data of thermomagnetic measurements for compounds **1**—**4** and **7**

1		2		3		4		7	
T/K	$\chi'_m \cdot 10^3$ /cm^3 mol^{-1}	*T*/K	$\chi'_m \cdot 10^3$ /cm^3 mol^{-1}	*T*/K	$\chi'_m \cdot 10^3$ /cm^3 mol^{-1}	*T*/K	$\chi'_m \cdot 10^3$ /cm^3 mol^{-1}	*T*/K	$\chi'_m \cdot 10^3$ /cm^3 mol^{-1}
289.608	2.861262	300.00	2.946	300.00	2.609	300.00	2.2214	293.029	1.125240
278.600	2.861262	270.00	3.288	270.00	2.939	270.00	2.5212	275.453	1.125240
275.704	2.812400	250.00	3.552	250.00	3.203	250.00	2.7491	272.211	1.125240
271.566	2.958985	230.00	3.878	230.00	3.501	230.00	3.0460	262.909	1.125240
268.372	2.861262	210.00	4.268	210.00	3.897	210.00	3.4000	253.561	1.042470
264.045	2.958985	190.00	4.742	190.00	4.350	190.00	3.8376	247.555	1.042470
252.263	3.105571	170.00	5.324	170.00	4.908	170.00	4.3572	235.351	1.042470
230.981	3.398742	150.00	6.062	150.00	5.614	150.00	5.0576	231.489	0.959700
213.707	3.496465	130.00	7.024	130.00	6.535	130.00	5.9533	215.178	0.959700
204.748	3.691912	110.00	8.353	110.00	7.787	110.00	7.1804	210.018	0.876930
170.457	4.033945	90.00	10.268	90.00	9.598	90.00	9.1664	195.529	0.959700
156.519	4.424839	80.00	11.588	80.00	10.837	80.00	10.4065	191.244	0.959700
138.707	4.424839	70.00	13.339	70.00	12.458	70.00	12.0595	178.718	0.876930
122.000	4.522563	60.00	15.621	60.00	14.665	60.00	14.3321	172.995	0.876930
114.252	4.815734	50.00	18.704	50.00	17.458	50.00	17.1683	162.857	0.794160
111.625	4.913458	40.00	23.361	40.00	21.796	40.00	21.5740	154.142	0.876930
104.000	5.206629	30.00	30.973	30.00	28.777	30.00	28.9115	139.712	0.794160
95.500	5.499799	25.00	37.112	25.00	34.320	25.00	34.8893	124.500	0.794160
88.500	5.597523	20.00	46.283	20.00	42.474	20.00	43.9367	116.672	0.711390
83.046	5.939556	17.00	54.337	17.00	49.473	17.00	51.9911	110.049	0.711390
		15.00	61.399	15.00	55.498	15.00	59.1945	97.000	0.794160
		13.00	70.557	13.00	63.123	13.00	68.5428	87.000	0.794160
		10.00	90.708	10.00	79.146	10.00	89.6840	82.000	0.794160
		8.00	111.85					80.386	0.794160
		7.00	126.68					79.836	0.794160
		6.00	145.58						
		5.00	170.155						

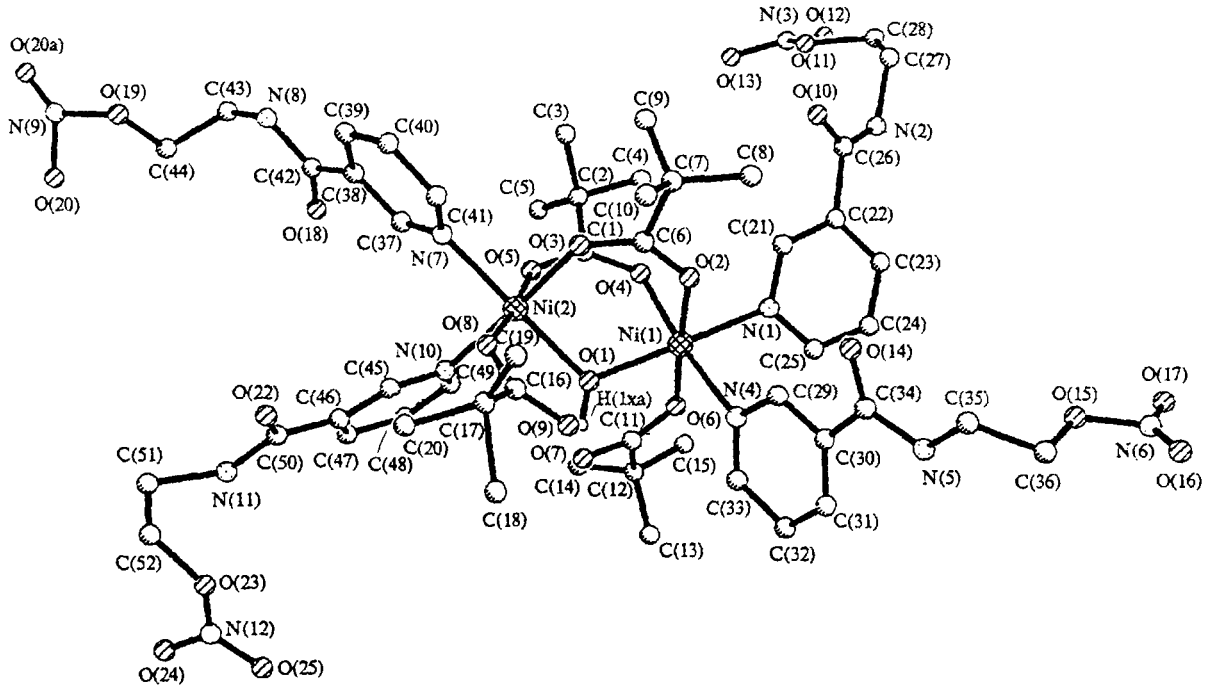

Fig. 5. Structure of the binuclear complex $Nic_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (**4**).

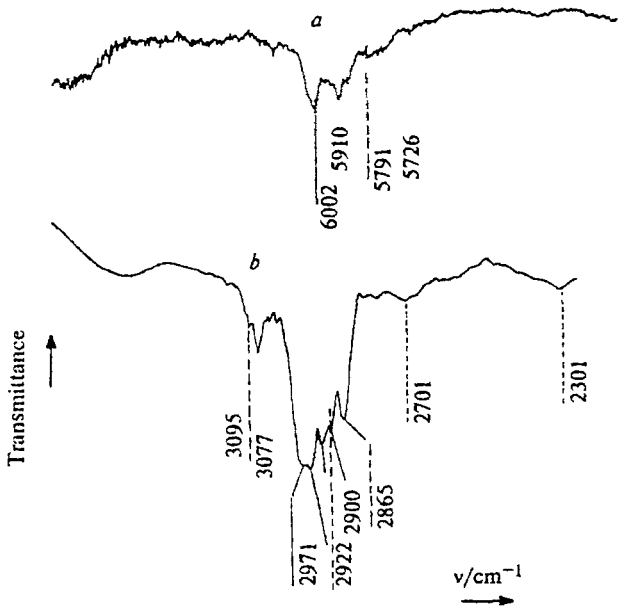

Fig. 6. IR spectrum of compound **2** in the 7000—4000 (*a*) and 4000—2000 (*b*) cm^{-1} regions.

(Fig. 7, Tables 11, 12), molecule **7** contains two metal atoms located at a nonbonded distance of 3.465(2) Å. The ligand environments about the Ni atoms are equivalent (nearly octahedral) as a result of bonding with the terminal molecule of pivalic acid (Ni—O, 2.142(5) Å; C—O, 1.176(9) and 1.341(11) Å), the carboxylate group (Ni—O, 2.069(5) Å; C—O, 1.242(8) and 1.267(9) Å), the pyridine ligand (Ni—N, 2.097(7) Å), the bridging O atom of the water molecule (Ni—O, 2.106(4) Å), and the two O atoms of the bridging pivalate ligands (Ni—O, 1.983(5)—1.992(5) Å). The two last-mentioned distances are substantially shorter than the values observed in the original compound **2**. According to the data of magnetic measurements (see Table 10), complex **7**, unlike **2**, is

Table 11. Bond lengths (*d*) in complex **7**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)...Ni(1a)	3.465(1)	O(1)—H(1a)	0.853(38)
Ni(1)—O(1)	2.106(4)	O(2)—C(1a)	1.248(9)
Ni(1)—O(2)	1.992(5)	O(3)—C(1)	1.241(8)
Ni(1)—O(3)	1.983(5)	O(4)—C(6)	1.341(11)
Ni(1)—O(5)	2.142(5)	O(5)—C(6)	1.176(9)
Ni(1)—O(7)	2.069(5)	O(6)—C(11)	1.242(8)
Ni(1)—N(1)	2.095(7)	O(7)—C(11)	1.267(9)
O(1)—H(1)	0.853(38)	C(1)—O(2a)	1.248(9)
O(1)—Ni(1a)	2.106(4)		

Table 12. Bond angles (ω) in complex **7**

Angle	ω/deg	Angle	ω/deg
O(1)—Ni(1)—O(2)	94.3(2)	O(1)—Ni(1)—O(3)	94.1(2)
O(2)—Ni(1)—O(3)	93.9(2)	O(1)—Ni(1)—O(5)	177.8(1)
O(2)—Ni(1)—O(5)	83.7(2)	O(3)—Ni(1)—O(5)	87.0(2)
O(1)—Ni(1)—O(7)	90.6(2)	O(2)—Ni(1)—O(7)	86.9(2)
O(3)—Ni(1)—O(7)	175.2(2)	O(5)—Ni(1)—O(7)	88.4(2)
O(1)—Ni(1)—N(1)	94.2(2)	O(2)—Ni(1)—N(1)	171.0(2)
O(3)—Ni(1)—N(1)	88.6(2)	O(5)—Ni(1)—N(1)	87.8(2)
O(7)—Ni(1)—N(1)	89.9(2)	Ni(1)—O(1)—Ni(1a)	110.7(3)
O(3)—C(1)—O(2a)	126.5(6)	O(4)—C(6)—O(5)	121.0(8)
O(6)—C(11)—O(7)	123.3(6)		

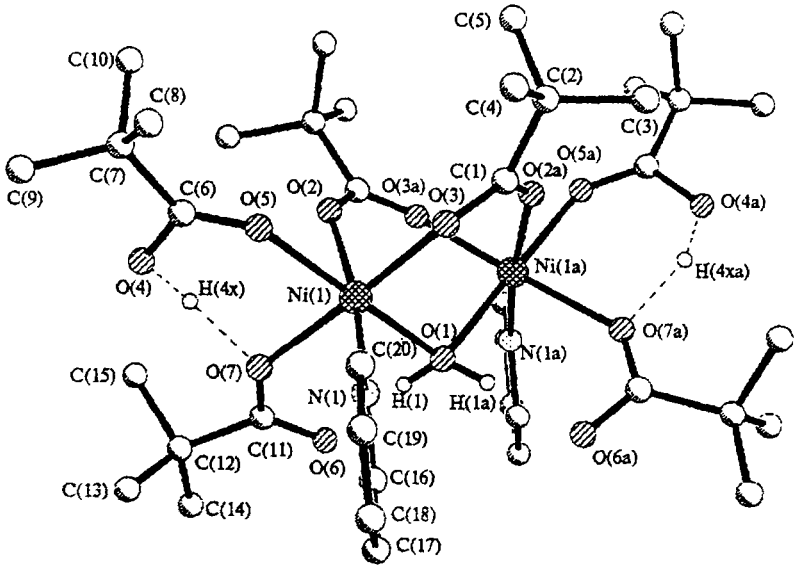

Fig. 7. Structure of the binuclear complex $Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (**7**).

antiferromagnetic and contains Ni^{II} atoms in the high-spin state S = 1. The magnetic moment (μ_{eff}/at. Ni) decreases monotonically from 1.90 to 0.84 μB in the temperature range of 293—79 K, which is adequately described within the framework of the Heisenberg—Dirac—Van Vleck model[23] with the parameter of the best approximation $-2J = 265$ cm^{-1}. Note that complex **7** differs in the magnetic behavior from isoelectronic complexes **6**, which are characterized by ferromagnetic exchange interactions. Compound **7** is similar in the exchange type to cation **5** for which the value of the exchange parameter is, however, substantially smaller ($-J = 5.5$ cm^{-1}, $\langle g \rangle = 2.17$, $\theta = 2.7(1)$ K).[18] The energy positions of the long-wave ligand field transitions in the electronic spectrum of complex **7** (see Table 3) agree with those expected for the $Ni^{II}O_5N$ chromophore and are similar to the positions of the corresponding bands for the known $Ni_2(glyox)(H_2O)_6 \cdot 4H_2O$ compound ($\nu \cdot 10^{-3}$, cm^{-1} = 8.93, 14.40, and 29.40; glyox is the O,N,O-tridentate bridging ligand).[24] The UV spectra of compounds **7** and **2—4** are very similar. In the near IR region of the spectrum of complex **7**, overtones of the stretching bands of the OH groups (see Table 3) are also observed. Therefore, the character of the spectra of binuclear compounds **2—4** and **7** is determined mainly by the contribution of transitions of the octahedral $Ni^{II}—NiO_4N_4$ or NiO_5N chromophores, respectively.

The formation of binuclear heterovalent nickel compounds **2—4** in the reactions of **1** with pyridine bases does not formally rule out the structure of the initial nonanuclear cluster with Ni^{II} and Ni^{III} atoms, all the more so since this process occurs also under inert conditions, although giving products in substantially lower yields. However, the presence of bridging O atoms and hydroxyl or aqua bridges in the nonanuclear clusters does not preclude, in principle, disproportionation of this complicated molecule (even if the molecule contains only Ni^{II} atoms, as was suggested in the second case) under the action of N-donors on heterovalent ions, for example, on Ni^{I} and Ni^{III}. Stabilization of Ni^{I} ions in the presence of oxo bridges is, apparently, difficult to achieve. As a result, they can undergo either intramolecular oxidation or oxidation under the action of atmospheric oxygen (when the reaction is carried out under ordinary conditions) to generate Ni^{II} ions. Therefore, in the case of both suggested formulas of complex **1**, the transformation into the complexes with Ni^{II} and Ni^{III} atoms can, in principle, occur.

In conclusion, note that the transformations of nickel pivalates demonstrate that the polynuclear system is the

Table 13. Crystallographic parameters of compounds

Parameter	$1 \cdot 4H_2O \cdot 0.5C_5H_{10}O_2 \cdot 0.5C_6H_6$	$2 \cdot 0.5C_6H_6$	$3 \cdot 2C_6H_6$	$4 \cdot THF \cdot 2H_2O$	7
Molecular formula	$C_{90}H_{148}Ni_9O_{38} \cdot 4H_2O \cdot 0.5C_5H_{10}O_2 \cdot 0.5C_6H_6$[a]	$C_{40}H_{57}N_4Ni_2O_9 \cdot 0.5C_6H_6$	$C_{48}H_{73}N_4Ni_2O_9 \cdot 2C_6H_6$	$C_{52}H_{73}N_{12}Ni_2O_{25} \cdot C_4H_8O \cdot 2H_2O$	$C_{40}H_{68}N_2Ni_2O_{13}$
Space group	*Pnma*	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	*C*/2*c*
a/Å	24.372(7)	11.553(4)	20.429(11)	13.808(4)	24.571(8)
b/Å	17.603(3)	11.617(3)	18.705(8)	15.470(4)	19.801(7)
c/Å	29.881(5)	20.172(4)	16.726(6)	20.653(5)	10.057(3)
α/deg		87.24(2)		93.30(2)	
β/deg		75.29(2)	99.22(2)	106.03(2)	96.68(2)
γ/deg		71.17(2)		108.48(2)	
V/Å^3	12820(5)	2476.7(11)	6309(5)	3970(2)	4860(3)
Z	4[b]	2	4[c]	2	4[c]
ρ_{calc}/g cm^{-3}	1.263	1.199	1.148	1.211	1.233
μ/cm^{-1}	13.62	8.11	6.48	5.51	8.32
θ—2θ scanning range/deg	3—56	2—56	2—55	2—46	2—54
Number of measured reflections	9865	9129	2699	7707	4586
Number of reflections with $I > 4.0\sigma$	5641	6847	2074	4332	3036
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0103F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0011F^2$	$w^{-1} = \sigma^2(F) + 0.0561F^2$	$w^{-1} = \sigma^2(F) + 0.0092F^2$
R	0.066	0.054	0.079	0.090	0.074
R_w	0.087	0.066	0.084	0.095	0.092

[a] The given formula involves only H atoms of the protonated and deprotonated pivalate groups. [b] The molecule is located on a crystallographic plane *m*. [c] The molecule is located on a crystallographic twofold axis.

Table 14. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B_{eq} \cdot 10^2/Å^2$) for cluster **1**

Atom	*x*	*y*	*z*	B_{eq}
Ni(1)	4274(1)	1/4	6648(1)	29(1)
Ni(2)	3153(1)	3303(1)	6177(1)	24(1)
Ni(3)	2511(1)	3280(1)	5312(1)	25(1)
Ni(4)	3086(1)	3274(1)	4453(1)	29(1)
Ni(5)	1943(1)	3368(1)	4169(1)	33(1)
O(1)	3755(3)	1/4	6111(3)	25(2)
O(2)	4362(2)	1362(3)	6712(2)	36(2)
O(3)	4850(4)	1/4	7177(4)	54(2)
O(4)	4396(6)	1/4	7797(5)	116(2)
O(5)	4927(4)	1/4	6227(4)	47(2)
O(6)	5390(5)	3462(7)	6428(6)	154(2)
O(7)	3672(4)	1/4	7137(3)	31(2)
O(8)	2933(3)	1/4	6688(3)	28(2)
O(9)	3516(3)	4053(3)	6581(2)	33(2)
O(10)	2477(2)	3928(3)	6291(2)	31(2)
O(11)	2654(4)	1/4	5838(3)	27(2)
O(12)	3229(2)	3798(3)	5518(2)	28(1)
O(13)	2065(2)	4058(3)	5625(2)	32(2)
O(14)	1839(3)	1/4	5238(3)	27(2)
O(15)	2382(2)	3733(3)	4702(2)	28(1)
O(16)	2978(3)	1/4	4972(3)	23(2)
O(17)	3537(3)	3992(3)	4821(2)	34(2)
O(18)	3713(4)	1/4	4285(3)	29(2)
O(19)	4093(4)	1/4	4981(3)	42(2)
O(20)	3215(3)	3911(3)	3914(2)	41(2)
O(21)	2556(4)	1/4	4092(3)	33(2)
O(22)	1527(4)	1/4	4528(3)	33(2)
O(23)	1449(4)	4907(5)	3687(3)	76(2)
O(24)	1346(3)	4203(4)	4310(2)	43(2)
O(25)	1480(3)	3126(4)	3636(2)	48(2)
O(26)	2339(3)	4134(3)	3758(2)	43(2)
C(1)	4929(9)	1/4	7516(9)	105(2)
C(12)	5417(7)	1/4	7832(6)	71(2)
C(13)	5232(12)	1/4	8276(8)	338(2)
C(14)	5785(8)	3090(12)	7696(8)	223(2)
C(2)	5276(10)	2777(8)	6234(7)	154(2)
C(21)	5923(6)	1/4	6043(5)	42(2)
C(22)	6334(6)	1/4	6415(5)	55(2)
C(23)	5956(7)	3193(7)	5763(5)	113(2)
C(3)	3158(6)	1/4	7075(4)	29(2)
C(31)	2768(6)	1/4	7469(4)	41(2)
C(32)	2412(5)	3193(7)	7434(4)	72(2)
C(33)	3079(7)	1/4	7905(5)	81(2)
C(4)	3980(4)	885(5)	6761(3)	32(2)
C(41)	4092(4)	199(5)	7058(3)	42(2)
C(42)	4113(7)	472(7)	7525(4)	104(2)
C(43)	4625(5)	−185(8)	6912(5)	93(2)
C(44)	3614(5)	−392(6)	7020(4)	75(2)
C(5)	3553(4)	4123(5)	5225(3)	31(2)
C(51)	3966(4)	4700(5)	5395(3)	33(2)
C(52)	4422(4)	4257(6)	5627(3)	44(2)
C(53)	3670(4)	5261(5)	5717(3)	48(2)
C(54)	4198(5)	5149(6)	4987(3)	55(2)
C(6)	2144(4)	4240(5)	6036(3)	32(2)
C(61)	1792(4)	4867(5)	6223(3)	36(2)
C(62)	1491(8)	4584(10)	6617(7)	190(2)
C(63)	1382(7)	5181(9)	5904(5)	142(2)
C(64)	2146(7)	5457(10)	6388(9)	220(2)
C(7)	4121(6)	1/4	4546(5)	40(2)
C(71)	4670(8)	1/4	4324(6)	69(2)
C(72)	4725(5)	1767(7)	4040(4)	76(2)
C(73)	5122(7)	1/4	4699(7)	94(2)
C(8)	1450(6)	1/4	4953(5)	35(2)
C(81)	865(5)	1/4	5128(5)	40(2)
C(82)	466(8)	1/4	4746(6)	113(2)
C(83)	791(5)	1803(8)	5400(5)	83(2)
C(9)	2857(5)	4233(5)	3695(3)	42(2)
C(91)	3014(5)	4772(7)	3321(4)	67(2)
C(92)	3614(7)	4807(12)	3261(7)	180(2)
C(93)	2888(8)	5587(7)	3508(5)	128(2)
C(94)	2681(7)	4669(8)	2909(4)	90(2)
C(10)	1177(5)	4713(6)	4053(4)	49(2)
C(101)	715(5)	5220(7)	4157(4)	68(2)
C(102)	229(7)	4909(14)	3934(9)	258(2)
C(103)	712(9)	5914(10)	3931(7)	183(2)
C(104)	679(8)	5345(12)	4650(5)	165(2)
C(11)	1327(8)	1/4	3496(5)	67(2)
C(111)	1094(12)	1/4	3018(10)	38(2)
C(11a)	731(10)	1/4	3195(9)	35(2)
C(112)	733(5)	1809(7)	2963(5)	81(2)
C(113)	321(12)	1/4	3466(12)	119(2)
C(13a)	1506(14)	1/4	2679(10)	80(2)
O(1k)	3810(14)	1/4	3441(12)	280(4)
C(1k)	3250(18)	1/4	3137(17)	223(4)
C(2k)	3623(17)	1/4	2578(15)	208(4)
C(3k)	3164(18)	1/4	2239(15)	219(4)
C(4k)	2574(16)	1/4	2435(15)	204(4)
C(5k)	2467(19)	1/4	2906(17)	104(4)
C(6k)	2906(14)	1/4	3199(13)	164(4)
C(7k)	4019(16)	3259(19)	2486(14)	132(4)
O(1w)	7408(7)	5694(11)	268(6)	107(4)
O(2w)	7320(10)	6958(14)	309(8)	100(4)

most stable structural fragment of these compounds, while we did not observe the formation of monomeric complexes at the ratio of the reagents used. In addition, binuclear three-bridged neutral hydroxocarboxylates with Ni atoms in different oxidation states were prepared for the first time. Finally, it was found that pyrolysis of complex **2** in xylene is accompanied by reduction of one metal atom to form three-bridged nickel(II) carboxylates.

Experimental

All operations associated with the synthesis of new complexes both in air and under an inert atmosphere were carried out, if required, with the use of anhydrous solvents. The IR spectra of the compounds were recorded on a Specord M-82 instrument (as KBr pellets or as Nujol mulls). The absorption spectra of solutions of compounds **1** and **4** in THF were measured on a Specord UV-VIS recording spectrophotometer in the 36000—12500 cm^{-1} region (the concentrations of the

Table 15. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B_{eq} \cdot 10^2/Å^2$) for complex **2**

Atom	x	y	z	B_{eq}
Ni(1)	1709(1)	1474(1)	1854(1)	55(1)
Ni(2)	3445(1)	1065(1)	3096(1)	46(1)
O(1)	693(2)	2606(2)	2688(1)	66(1)
O(2)	1946(2)	2585(2)	3367(1)	58(1)
O(3)	1452(2)	21(2)	2390(1)	63(1)
O(4)	2351(2)	−25(2)	3244(1)	65(1)
O(5)	1828(3)	2993(2)	1311(1)	74(1)
O(6)	3613(3)	3167(2)	1440(2)	81(1)
O(7)	4990(2)	−486(2)	2889(1)	60(1)
O(8)	5301(3)	−705(3)	1775(2)	102(1)
O(9)	3433(2)	1251(2)	2070(1)	49(1)
N(1)	−19(3)	1754(3)	1583(2)	75(1)
N(2)	2681(3)	328(3)	970(2)	73(1)
N(3)	3404(3)	875(3)	4143(2)	55(1)
N(4)	4632(3)	2154(3)	2992(2)	56(1)
C(1)	922(3)	2942(3)	3201(2)	48(1)
C(2)	−160(3)	3896(3)	3693(2)	73(1)
C(3)	−366(5)	3393(5)	4388(3)	89(1)
C(4)	252(5)	4988(4)	3742(4)	109(1)
C(5)	−1333(4)	4200(5)	3464(3)	86(1)
C(6)	1684(3)	−346(3)	2950(2)	52(1)
C(7)	1094(3)	−1281(3)	3300(2)	78(1)
C(8)	120(4)	−1438(4)	3011(3)	150(1)
C(9)	543(4)	−942(4)	4031(3)	246(1)
C(10)	2087(4)	−2437(4)	3297(4)	256(1)
C(11)	2617(4)	3541(3)	1250(2)	68(1)
C(12)	2314(4)	4789(3)	914(2)	91(1)
C(13)	2170(5)	5708(4)	1395(4)	215(1)
C(14)	1162(5)	5100(5)	659(4)	143(1)
C(15)	3339(5)	4794(4)	311(4)	106(1)
C(16)	5526(3)	−1062(3)	2331(2)	61(1)
C(17)	6526(3)	−2300(3)	2330(2)	77(1)
C(18)	6129(5)	−2923(4)	3024(3)	77(1)
C(19)	7705(4)	−2131(4)	2275(4)	99(1)
C(20)	6515(5)	−3154(4)	1799(3)	104(1)
C(21)	−383(4)	849(4)	1456(3)	117(1)
C(22)	−1441(4)	1020(4)	1230(3)	171(1)
C(23)	−2160(4)	2163(4)	1126(3)	191(1)
C(24)	−1805(4)	3095(4)	1263(3)	135(1)
C(25)	−741(4)	2885(3)	1488(2)	90(1)
C(26)	2796(4)	758(4)	345(2)	89(1)
C(27)	3504(4)	45(4)	−236(2)	114(1)
C(28)	4088(4)	−1133(4)	−179(3)	125(1)
C(29)	3975(4)	−1589(4)	447(3)	113(1)
C(30)	3301(4)	−853(3)	1008(2)	91(1)
C(31)	3073(3)	1825(3)	4569(2)	70(1)
C(32)	2951(4)	1730(4)	5257(2)	94(1)
C(33)	3140(4)	645(4)	5533(2)	104(1)
C(34)	3473(4)	−364(4)	5115(2)	92(1)
C(35)	3596(3)	−221(3)	4422(2)	69(1)
C(36)	4253(3)	3328(3)	2854(2)	74(1)
C(37)	4963(4)	4068(3)	2801(3)	107(1)
C(38)	6155(4)	3558(4)	2901(3)	137(1)
C(39)	6580(4)	2372(4)	3030(3)	119(1)
C(40)	5795(3)	1690(3)	3082(2)	79(1)
C(3a)	−1043(5)	3104(5)	3999(5)	282(1)
C(4a)	137(5)	4356(5)	4261(4)	187(1)
C(5a)	−858(5)	4869(5)	3285(5)	241(1)
C(13a)	3444(5)	5297(5)	878(5)	189(1)
C(14a)	1094(5)	5619(5)	1302(5)	157(1)
C(15a)	2278(5)	4514(5)	184(5)	209(1)
C(18a)	7232(5)	−2385(5)	2842(5)	255(1)
C(19a)	7499(5)	−2602(5)	1572(5)	200(1)
C(20a)	6067(5)	−3175(5)	2386(5)	255(1)
C(3b)	4390(5)	5826(5)	4692(4)	216(1)
C(2b)	5780(5)	5222(5)	5258(4)	218(1)
C(1b)	5106(5)	6013(4)	4981(4)	249(1)
H(1)	4126(5)	1211(5)	1802(5)	82(1)

solutions were 10^{-1}—10^{-2} mol L^{-1}; 1.0-, 0.2-, and 0.1-cm cells were used). The diffuse reflection spectra of polycrystalline samples of the compounds under study were measured on a Hitachi-300 recording spectrophotometer in the 50000—4000 cm^{-1} region. The IR spectra of complex **2** in the near IR region were obtained on a Nicolet Magna-750 Fourier IR spectrometer. The static magnetic susceptibilities χ'_m of samples of **1** and **7** were measured using the Faraday method in the temperature range of 77—300 K on an instrument at the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.[25] The static magnetic susceptibilities χ'_m of samples of **2**—**4** were measured in the temperature range of 5—300 K on a SKVID magnetometer at the University of Santiago de Compostela. The effective magnetic moments were calculated according to the following formula:

$$\mu_{eff} = \sqrt{8\chi'_m T}\,.$$

Cluster $Ni_9(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(HOOCCMe_3)_4(OOCCMe_3)_{12}$ (1). A solution of pivalic acid (20 g, 0.2 mol) in water (20 mL) and KOH (11.2 g, 0.2 mol; $KOOCCMe_3$ can be prepared preliminarily and then dissolved in water) were added to a solution of $NiCl_2 \cdot 6H_2O$ (23.8 g, 0.1 mol) in water (20 mL). The pale-green coagulated precipitate that formed was filtered off and extracted with CH_2Cl_2 (70—100 mL). The green solution was concentrated to 5—10 mL and cooled to −5 °C. The finely crystalline precipitate of cluster **1** that formed was separated by decantation and dried *in vacuo*. The yield was 19.7—22.5 g (70—80%). The complex was twice recrystallized from hexane, and large prismatic crystals of cluster **1** were separated. The yield of the pure product was 14.1—15.5 g (50—55%). Found (%): C, 45.4; H, 6.2. $C_{90}H_{151}Ni_9O_{38}$. Calculated (%): C, 45.62; H, 6,38. IR, ν/cm^{-1}: 554 w, 628 m, 801 m, 851 m, 882 m, 906 m, 943 w, 1030 m, 1104 w, 1234 s, 1264 w, 1326 m, 1369 v.s, 1425 v.s, 1493 v.s, 1573 v.s, 1610 v.s, 1672 s, 1703 v.s, 2882 m, 2932 s, 2969 v.s, 3457 s.

Complexes $L_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (L = Py (2), Lut (3), or Nic (4)). Freshly distilled pyridine (2.37 g, 30 mmol) was added to a solution of cluster **1** (2.52 g, 1 mmol) in benzene or toluene (20 mL), and the reaction mixture was stirred at ~20 °C for 0.5 h after which the solution developed a stable blue color. The solution was concentrated to dryness at 50 °C/0.1 Torr. The dry residue was extracted with benzene or toluene (4×20 mL) until the extract became colorless. The blue extract was concentrated to 10—15 mL and cooled to 5 °C. The blue prismatic crystals that precipitated were separated by decantation and dried *in vacuo*. The yield of complex **2** was 3.22 g (80%). Found (%): C, 55.9; H, 6.6; N, 6.4. $C_{40}H_{57}N_4Ni_2O_9$. Calculated (%): C, 56.18; H, 6.67; N, 6.55. IR (Nujol mulls), ν/cm^{-1}: 419 m, 431 m, 554 w, 586 w, 604 s, 630 m, 652 w, 676 w, 697 s, 755 s, 933 w, 984 w, 1012 m, 1039 s, 1072 m, 1100 m.br., 1150 m, 1219 s, 1357 v.s,

Table 16. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B_{eq} \cdot 10^2/Å^2$) for complex 3

Atom	*x*	*y*	*z*	B_{eq}
Ni(1)	553(1)	7137(1)	1784(1)	39(1)
O(1)	1376(4)	6467(5)	2119(5)	50(3)
O(2)	1039(5)	5846(5)	3121(5)	60(3)
O(3)	0	6532(5)	1/4	41(3)
O(4)	936(4)	7732(4)	2729(5)	51(3)
O(5)	−226(5)	7772(4)	1354(5)	42(3)
N(1)	1143(6)	7745(5)	1131(6)	43(3)
N(2)	281(6)	6491(5)	755(5)	34(3)
C(1)	1454(7)	6050(7)	2719(8)	43(3)
C(2)	2148(8)	5729(7)	2922(8)	52(3)
C(3)	2224(10)	5125(12)	2416(12)	181(4)
C(4)	2310(9)	5543(10)	3808(8)	94(4)
C(5)	2689(9)	6286(12)	2771(14)	161(4)
C(6)	777(9)	7932(7)	3415(9)	51(3)
C(7)	1301(8)	8350(7)	4004(9)	63(3)
C(8)	971(19)	8987(19)	4410(21)	84(6)
C(9)	1837(20)	8665(20)	3545(22)	89(6)
C(10)	1575(17)	7786(16)	4683(19)	68(6)
C(8a)	971(19)	8696(18)	4697(20)	79(6)
C(9a)	1590(18)	8970(18)	3528(20)	73(6)
C(10a)	1834(19)	7807(19)	4302(21)	87(6)
C(11)	1798(9)	7795(8)	1337(9)	59(3)
C(12)	2206(9)	8179(9)	903(10)	73(4)
C(13)	1920(10)	8559(10)	218(10)	82(4)
C(14)	1255(9)	8510(9)	−1(10)	78(4)
C(15)	871(9)	8124(8)	464(9)	67(3)
C(16)	2896(14)	8131(17)	1128(18)	98(6)
C(16a)	892(16)	8916(16)	−676(16)	92(6)
C(17)	2356(10)	8997(10)	−280(11)	118(4)
C(18)	−343(8)	6379(6)	442(7)	42(3)
C(19)	−569(7)	5996(6)	−302(7)	38(3)
C(20)	−1287(7)	5908(8)	−607(8)	64(3)
C(21)	−66(8)	5711(6)	−681(7)	37(3)
C(22)	−251(8)	5302(7)	−1496(7)	60(3)
C(23)	582(8)	5821(7)	−369(8)	46(3)
C(24)	733(8)	6227(7)	368(8)	46(3)
C(1b)	0	10756(32)	1/4	117(7)
C(2b)	338(18)	10676(23)	1792(23)	114(6)
C(3b)	558(27)	10025(27)	1673(32)	212(7)
C(4b)	309(16)	9541(23)	2113(19)	99(6)
C(5b)	0	9536(16)	1/4	17(5)
C(6b)	−192(32)	10243(28)	2588(37)	263(7)
C(7b)	706(25)	2683(20)	3242(23)	103(6)
C(8b)	1001(25)	2702(25)	2690(32)	146(6)
C(9b)	674(22)	2623(22)	1994(26)	103(6)
C(10b)	214(24)	2637(22)	1675(24)	102(6)
C(11b)	0	2661(29)	1/4	106(7)
C(12b)	123(20)	2695(16)	3055(17)	55(6)
H(3xa)	0	6041(55)	1/4	89(9)

1370 v.s, 1414 v.s, 1448 v.s, 1482 s, 1531 s, 1576 s, 1613 v.s, 3047 w, 3270 w. Compound **3** was prepared analogously by using 3,4-lutidine (2.68 g, 25 mmol). Complex **4** was synthesized with the use of a solution of nicorandil (4.24 g, 20 mmol) in THF (30 mL), and extraction was carried out with the use of a 1 : 1 THF—benzene mixture. The yields of complexes **3** and **4** were 3.64 g (72%) and 2.69 g (40%), respectively. For **3**, found (%): C, 60.4; H, 7.2; N, 6.1. $C_{48}H_{73}N_4Ni_2O_9$. Calculated (%): C, 59.60; H, 7.55; N, 5.79. IR (Nujol mulls), ν/cm^{-1}: 410 m, 520 w, 530 w, 600 m, 670 w, 720 m, 782 m, 822 m, 858 m, 1010 w, 1070 m, 1182 m, 1220 m, 1302 w, 1350 m, 1362 m, 1408 s, 1416 m, 1479 s, 1486 m, 1522 m, 1605 s, 3066 w, 3322 w. For **4** · THF · $2H_2O$, found (%): C, 45.3; H, 5.7; N, 11.2. $C_{52}H_{73}N_{12}Ni_2O_{25}$. Calculated (%): C, 45.11; H, 5.70; N, 11.27. IR (Nujol mulls), ν/cm^{-1}: 480 w, 600 m, 640 m, 698 s, 740 m, 820 m, 850 s, 890 s, 1026 m, 1040 m, 1102 m, 1160 m, 1182 m, 1220 m, 1280 s, 1315 s, 1410 s, 1480 s, 1540 s, 1604 s, 1610 s, 1638 s, 3040 m, 3280 m, 3401 w.

Complex $Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (7). A blue solution of complex **2** (1.79 g, 2 mmol) in *m*-xylene (30 mL) was boiled for 1 h until the solution developed a green color. Then the solution was slowly cooled to ~20 °C. The green needle-like crystals that precipitated were separated from the mother liquor by decantation, washed with cold hexane (0—5 °C), and recrystallized from benzene. The yield of complex **7** was 0.52—0.59 g (35—40%). Found (%): C, 54.0; H, 7.6; N, 3.2. $C_{40}H_{68}N_2Ni_2O_{13}$. Calculated (%): C, 53.25; H, 7.54; N, 3.11. IR (Nujol mulls), ν/cm^{-1}: 430 m, 610 w, 690 m, 720 w, 750 w, 782 w, 886 w, 1038 w, 1060 w, 1140 w, 1220 m, 1354 m, 1418 s, 1448 s, 1478 m, 1600 s, 1690 s, 1705 w, 3048 w, 3415 w.

X-ray diffraction analysis. Single crystals of **1** · $4H_2O$ · $0.5C_6H_6$ · $0.5Me_3CCOOH$ were obtained upon storage of a hexane extract of the complex with addition of several drops of benzene at −15 °C for 2—4 h. Crystals of compound **4** suitable for X-ray diffraction study were grown by evaporation of a solution of the complex in a 10 : 1 THF—water mixture (solvate **4** · THF · $2H_2O$). Crystals of compounds **2**, **3**, and **7** were grown by slow cooling of concentrated benzene solutions (50 °C) to ~20 °C (for **2** and **3**, solvates with 0.5 and 2 benzene molecules were obtained). The X-ray intensity data sets were collected on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, T = 22 °C (for **2**, **4**, and **7**), 0 °C (for **3**), and −120 °C (for **1**)). The crystallographic parameters and the details of the refinement of all the structures are given in Table 13.

The structures of complexes **1** · $4H_2O$ · $0.5C_6H_6$ · $0.5Me_3CCOOH$, **2** · $0.5C_6H_6$, **3** · $2C_6H_6$, **4** · THF · $2H_2O$, and **7** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents and the pyridine ligands were calculated geometrically and refined using the riding model. The H atoms of the bridging hydroxyl groups in compounds **2** and **3**, of the water molecules, and of the HOOC groups of the coordinated acid molecule in compound **7** were located from the difference Fourier syntheses and refined isotropically. For all the structures, absorption corrections were applied.[26] In **2** · $0.5C_6H_6$ and **3** · $2C_6H_6$, the benzene molecules of solvation are disordered. Both positions of these molecules were revealed. The refinement of their occupancies gave values close to 0.5. In compound **4**, one nicorandil ligand and the *tert*-butyl group of one OOCR fragment are disordered over two sites with equal occupancies (0.5). The disorder of some *tert*-butyl substituents in the pivalate fragments is also observed in compounds **1**, **2**, and **3**. In the structure of **3**, the methyl groups of the lutidine fragment are also disordered. In compound **1**, benzene mol-

Table 17. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B_{eq} \cdot 10^2/Å^2$) for complex **4**

Atom	x	y	z	B_{eq}
Ni(1)	1728(2)	4711(2)	2418(1)	33(1)
Ni(2)	1552(2)	6620(2)	3313(1)	33(1)
O(1)	1919(8)	6112(7)	2493(5)	32(2)
O(2)	200(9)	4377(8)	2405(5)	37(2)
O(3)	185(9)	5520(8)	3106(6)	45(2)
O(4)	2171(9)	4676(8)	3436(5)	45(2)
O(5)	2449(9)	6075(7)	4002(5)	38(2)
O(6)	3267(8)	4982(8)	2440(5)	40(2)
O(7)	3850(9)	6533(9)	2498(6)	54(2)
O(8)	670(9)	7290(8)	2702(5)	41(2)
O(9)	619(9)	6769(8)	1667(5)	46(2)
O(10)	−404(10)	1592(9)	3277(6)	52(2)
O(11)	1189(12)	782(11)	4778(8)	88(2)
O(12)	2365(18)	116(15)	5279(12)	162(2)
O(13)	2564(18)	1697(17)	5538(14)	183(3)
O(14)	−1994(10)	3194(10)	336(6)	69(2)
O(15)	−2683(16)	1087(14)	−1336(12)	154(2)
O(16)	−3696(22)	367(19)	−2302(16)	89(3)
O(16a)	−3851(26)	3(23)	−1781(19)	139(3)
O(17)	−2534(22)	−211(20)	−1499(16)	102(3)
O(17a)	−2755(25)	219(23)	−2224(20)	138(3)
O(18)	3501(10)	8468(9)	5903(6)	61(2)
O(19)	2818(20)	10336(19)	7199(16)	212(3)
O(20)	4126(26)	11535(24)	7475(20)	158(3)
O(21)	3526(26)	10741(25)	8269(21)	165(3)
O(22)	2517(13)	10366(11)	3664(11)	119(2)
O(23)	4320(23)	11932(20)	2837(17)	237(3)
O(24)	5777(22)	12917(23)	3083(19)	228(3)
O(25)	4062(16)	12487(14)	1949(11)	157(3)
N(1)	1525(11)	3281(9)	2339(7)	40(2)
N(2)	492(12)	596(10)	3306(7)	47(2)
N(3)	2074(19)	788(19)	5297(14)	143(3)
N(4)	1210(10)	4544(9)	1319(6)	34(2)
N(5)	−1722(11)	2928(10)	−710(7)	48(2)
N(6)	−3022(18)	259(17)	−1769(13)	121(2)
N(7)	1112(10)	7130(9)	4125(6)	34(2)
N(8)	2359(12)	8592(10)	6468(7)	51(2)
N(9)	3190(22)	11183(18)	7722(15)	172(3)
N(10)	2916(11)	7868(9)	3540(7)	41(2)
N(11)	4302(16)	11180(13)	3942(13)	109(2)
N(12)	4929(25)	12342(23)	2562(20)	240(3)
C(1)	2404(12)	5241(10)	3973(7)	31(2)
C(2)	2673(16)	4894(13)	4635(9)	58(2)
C(3)	1650(21)	4778(21)	4937(17)	178(2)
C(4)	2593(19)	3919(15)	4595(13)	107(2)
C(5)	3549(23)	5451(21)	5136(18)	217(3)
C(6)	−233(12)	4739(10)	2730(8)	30(2)
C(7)	−1421(14)	4201(12)	2681(9)	55(2)
C(8)	−1821(16)	3230(14)	2251(11)	78(2)
C(9)	−1483(22)	4032(19)	3398(14)	151(2)
C(10)	−2105(20)	4647(18)	2297(16)	147(2)
C(11)	3952(12)	5757(11)	2528(7)	33(2)
C(12)	5119(17)	5801(15)	2627(12)	80(2)
C(13)	5408(21)	6002(19)	2056(14)	136(2)
C(14)	5841(22)	6350(20)	3333(16)	166(2)
C(15)	5225(21)	4848(18)	2748(16)	156(2)
C(16)	363(13)	7230(11)	2077(8)	39(2)
C(17)	−425(15)	7747(13)	1754(10)	59(2)
C(18)	−145(25)	8134(23)	1082(20)	75(3)
C(19)	−1565(26)	7231(26)	1623(20)	98(3)
C(20)	390(26)	8870(24)	2075(21)	86(3)
C(19a)	−98(23)	8627(21)	2230(17)	51(3)
C(18a)	−567(25)	7722(24)	1030(19)	79(3)
C(20a)	−1415(27)	7340(25)	2070(22)	100(3)
C(21)	1001(12)	2771(11)	2691(8)	34(2)
C(22)	918(13)	1852(11)	2689(8)	39(2)
C(23)	1350(15)	1470(12)	2278(10)	59(2)
C(24)	1919(15)	2018(13)	1906(10)	65(2)
C(25)	1946(15)	2881(13)	1925(10)	60(2)
C(26)	256(13)	1325(11)	3130(8)	41(2)
C(27)	−46(15)	10(12)	3733(10)	58(2)
C(28)	647(17)	−186(14)	4276(11)	84(2)
C(29)	201(12)	4057(11)	994(8)	35(2)
C(30)	−258(12)	3801(10)	268(8)	34(2)
C(31)	483(13)	4134(11)	−82(8)	41(2)
C(32)	1521(14)	4660(12)	256(9)	47(2)
C(33)	1860(13)	4866(11)	949(8)	35(2)
C(34)	−1355(14)	3286(12)	−9(9)	47(2)
C(35)	−2901(15)	2474(13)	−1043(10)	65(2)
C(36)	−3172(21)	1775(18)	−1633(15)	39(3)
C(36a)	−3247(27)	1504(24)	−994(20)	101(3)
C(37)	1852(12)	7503(10)	4724(7)	31(2)
C(38)	1671(12)	7828(10)	5302(8)	34(2)
C(39)	592(13)	7752(11)	5220(8)	41(2)
C(40)	−179(13)	7364(12)	4590(8)	46(2)
C(41)	106(12)	7061(10)	4058(8)	32(2)
C(42)	2533(12)	8293(11)	5892(8)	37(2)
C(43)	3212(15)	9017(14)	7103(10)	70(2)
C(44)	3639(24)	9960(20)	7128(16)	56(3)
C(44a)	2907(26)	9339(24)	7570(24)	117(3)
C(45)	2819(13)	8677(10)	3555(8)	36(2)
C(46)	3661(13)	9481(12)	3796(9)	46(2)
C(47)	4696(15)	9460(13)	4023(10)	62(2)
C(48)	4845(15)	8622(13)	4028(11)	69(2)
C(49)	3921(14)	7803(12)	3800(9)	54(2)
C(50)	3458(17)	10318(15)	3764(12)	87(2)
C(51)	4230(24)	12113(20)	4035(18)	173(2)
C(52)	4058(25)	12387(25)	3490(20)	227(2)
O(1s)	7819(25)	443(23)	1214(19)	307(3)
C(1s)	8525(26)	−29(24)	839(21)	217(3)
C(2s)	9443(26)	284(24)	274(21)	221(3)
C(3s)	9325(26)	1240(24)	524(20)	218(3)
C(4s)	8319(26)	1264(24)	801(21)	210(3)
O(2s)	4669(23)	3021(21)	324(17)	269(3)
O(3s)	4878(21)	−155(19)	9020(16)	237(3)

ecules of solvation and molecules of pivalic acid are disordered. In these cases, the occupancies of the alternative positions are approximately equal to 0.5. All calculations were carried out with the use of the SHELXTL PLUS program package (PC version)[27]. The atomic coordinates of complexes **1**—**4** and **7** are given in Tables 14—18, respectively. The principal geometric parameters are given in Tables 1, 2, 4—9, 11, and 12, respectively.

We thank Prof. B. V. Lokshin for recording the spectra of complex **2** in the near IR region. X-ray diffraction studies of all the crystals were carried out in

Table 18. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B_{eq} \cdot 10^2/Å^2$) for complex **7**

Atom	*x*	*y*	*z*	B_{eq}
Ni(1)	561(1)	7339(1)	1605(1)	44(1)
O(1)	0	6734(3)	1/4	49(1)
O(2)	647(2)	8009(3)	3091(5)	62(1)
O(3)	−16(2)	7866(3)	520(5)	60(1)
O(4)	1883(3)	7767(4)	2158(9)	121(1)
O(5)	1145(2)	7967(3)	770(5)	58(1)
O(6)	802(2)	6098(3)	3863(6)	74(1)
O(7)	1210(2)	6823(3)	2637(5)	60(1)
N(1)	591(2)	6692(3)	−33(7)	63(1)
C(1)	−426(3)	8145(3)	885(6)	49(1)
C(2)	−672(3)	8750(4)	25(7)	62(1)
C(3)	−1276(4)	8680(7)	−276(11)	126(1)
C(4)	−409(5)	8840(7)	−1264(10)	123(1)
C(5)	−566(6)	9385(5)	896(12)	136(2)
C(6)	1596(3)	8121(4)	1178(7)	67(1)
C(7)	1918(4)	8671(5)	595(9)	84(1)
C(8)	1725(6)	8806(10)	−752(11)	204(2)
C(9)	2513(4)	8561(8)	793(12)	150(2)
C(10)	1832(7)	9307(7)	1487(15)	173(2)
C(11)	1221(3)	6374(3)	3538(7)	50(1)
C(12)	1780(3)	6142(4)	4189(8)	62(1)
C(13)	2121(5)	5936(7)	3133(11)	147(1)
C(14)	1752(4)	5581(6)	5145(11)	111(1)
C(15)	2042(5)	6747(7)	4956(12)	139(1)
C(16)	590(3)	6026(5)	75(10)	88(1)
C(17)	635(4)	5610(6)	−1062(14)	130(1)
C(18)	681(4)	5965(8)	−2330(13)	143(1)
C(19)	687(4)	6587(6)	−2377(11)	108(1)
C(20)	638(4)	6963(5)	−1272(8)	81(1)
H(1)	256(19)	6535(20)	2997(25)	45(3)
H(4x)	1615(20)	7373(21)	3344(25)	50(3)

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