Articles

Bi- and Mononuclear Nickel(II) Trimethylacetate Complexes with Pyridine Bases as Ligands

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Reaction of the nine-nuclear cluster $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3$ $(OOCCMe_3)_{12}$ (**1**) with pyridine results in the binuclear species $Py_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (**2**). Thermolysis of **2** at 100−140 °C in toluene or xylene leads to complex $Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (**3**). This complex can be converted back in **2** by the reaction of **3** with 2 equiv of pyridine. Thermolysis of solid **3** in vacuo at 170 °C gives the binuclear tetra-bridged trimethylacetate $Py_2Ni_2(\mu\text{-}OOCCMe_3)_4$ (**4**) which can be reverted in **3** by reaction with 1 equiv of H_2O and 2 equiv of $HOOCCMe_3$. Compound **4** might be also prepared by the reaction of the complexes $L_2Ni_2(\mu\text{-}OOCCMe_3)_4$ (L = 2,3-lutidine (**5**), Et_3N (**6**)) with pyridine at 40−80 °C in hexane or benzene solution. Complexes **5** and **6** are formed in an one-step reaction by interaction of complex **1** and ligand L. Complex $Dipy_2Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (**7**), an isoelectronic analogue of complex **2**, was prepared by reacting **1** with Dipy. Thermolysis of solid **7** at 170 °C in vacuo gives monomer $DipyNi(OOCCMe_3)_2$ (**8**). Hetero-ligand complex $DipyNi(NH_2Ph)(OOCCMe_3)_2$ (**9**) was obtained upon the reaction of $PhNH_2$ with complex **7** at 20 °C in benzene or MeCN. Reaction of **1** with α,α',α''-tripyridyl leads to the formation of the monomeric $TerpyNi(OOCCMe_3)_2$ (**10**). Complexes **4**−**10** were characterized with X-ray data. Magnetic properties of the synthesized complexes are discussed.

Introduction

Binuclear carboxylate-bridged units have been found to be important structural units in different metalloenzymes. For example, a μ-carboxylate-bridged dimetal species exist in iron-containing hemerythrins and ribonucleatide reductase and in manganese containing catalases.[1] Similar fragments can be also found in none-redox enzymes with homo- and hetero-bimetallic cores.[1] Dinickel moiety with two nickel atoms being held together via two carboxylate bridging oxygen atoms of a carbamylated lysine residue has been found in urease.[2] It is generally agreed that the carboxylate complexes of the 3d elements including several examples of nickel derivatives[3−10] play an important role in biochemistry. However, only a few of nickel carboxylate complexes were characterized structur-

ally.[7,10] Trimethylacetate complexes seem to be very convenient objects for different chemical and biochemical modeling studies due to their high solubility in both aqueous and organic media. The availability of well-characterized and soluble (in organic solvents) Ni compounds can give a new stimulus for the development of both the basic researches and applied nickel chemistry, e.g., designing artificial biocatalysts or molecular magnetics. In this context, a study aimed at syntheses of nickel complexes with alkylcarboxylate and pyridine ligands was initiated by our group.

Trimethylacetate was the alkylcarboxylate ligand of choice because of its compatibility with common organic solvents. Pyridine (Py), 2,3-lutidine (Lut), α,α'-dipyridyl (Dipy), and α,α',α''-tripyridyl (Terpy) were chosen to inspect the influence of the ligand dentaty on the formed complex structure.

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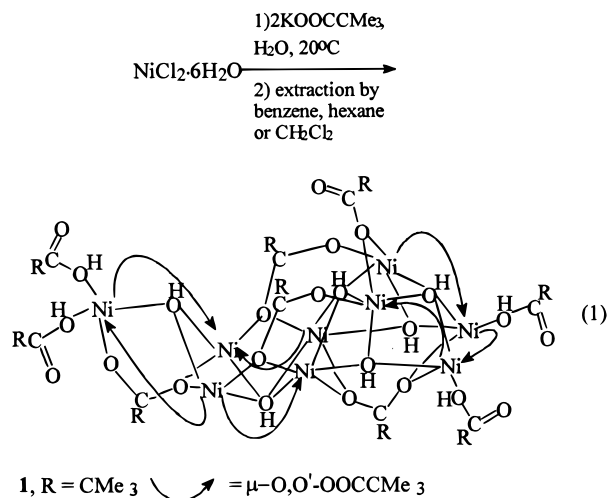‡ Siberian Branch of Russian Academy of Sciences.
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(2) Jabri, E.; Carr, M. B.; Hausinger, R. P.; Karplus, P. A. *Science* **1995**, *268*, 998.
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Results and Discussion

Nine-nuclear nickel cluster $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ (**1**) was used as a starting compound in the syntheses of entitled complexes. Cluster **1**, a substance readily soluble both in organic and aqueous media and characterized with X-ray data, is readily accessible from the reaction between $NiCl_2\cdot6H_2O$ and $KOOCCMe_3$ (or equimolar mixture of KOH and $HOOCCMe_3$) in water.[11] After the extraction of reaction mixture by hexane, benzene or dichlorometane the nine-nuclear antiferromagnetic cluster **1** can be isolated in a yield of 75–90% (eq 1).

$$NiCl_2\cdot6H_2O \xrightarrow[\substack{\text{2) extraction by} \\ \text{benzene, hexane} \\ \text{or } CH_2Cl_2}]{\substack{\text{1)}2KOOCCMe_3, \\ H_2O, 20^\circ C}}$$

(1)

**1**, R = CMe_3 ⟍↗ = μ–O,O'-$OOCCMe_3$

Reactions between cluster **1** and organic bases (Py, 3,4-lutidine or *N*-nitroxyethylnicotinamide) afforded the only product — binuclear ferromagnetic complexes $L_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (L = Py (**2**), 3,4-Lut or Nic),[13] regardless of the reagent ratio[11] (eq 2).

$Ni_9(HOOCCMe_3)_4(\mu\text{-}OOCCMe_3)_{12}(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3$

1

(2)

L = Py (**2**), 3,4-Lut, Nic
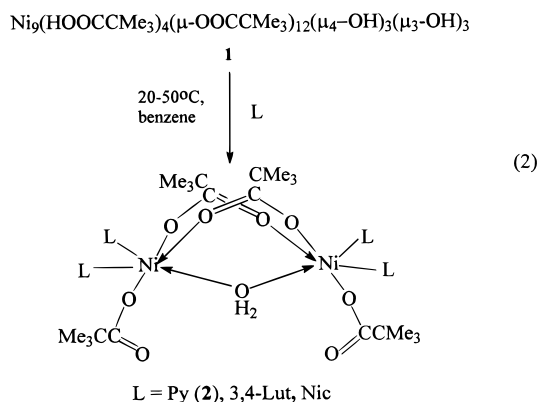
Two pyridine ligands of complex **2** are smoothly substituted at the thermolysis of **2** in toluene or *o*-xylene (100–140 °C) by

two neutral trimethylacetic acid molecules giving rise to binuclear complex $Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOC\text{-}CMe_3)_2(\mu\text{-}OH_2)$ (**3**) (eq 3).

(3)

L' = $HOOCCMe_3$
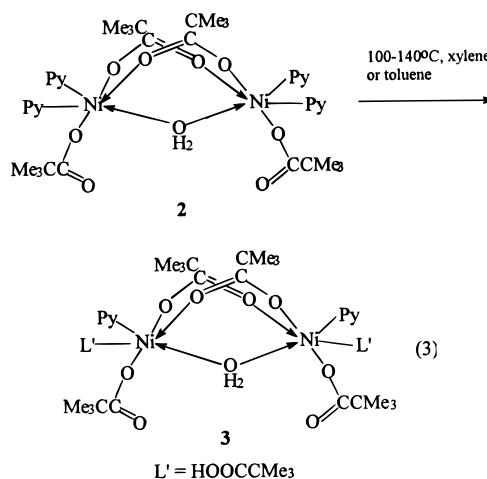
Both Ni atoms in complex **3** have the same octahedral ligand environment. As a consequence of that, both metallic centers have the same electronic configuration and the complex with Ni···Ni distance equal to 3.465(2) Å exhibits antiferromagnetic behavior.[13] Both complex **2** and complex **3** contain rather uncommon H_2O bridging group. It is remarkable that the bridge with "oxane" oxygen atom was not cleaved under the condition of complex **2** thermolysis suggesting the bridging H_2O molecule to be bound to two Ni atoms more strongly than monodentately coordinated and more basic Py molecules having been substituted probably due to $HOOCCMe_3$ ligand disproportionation. Surprisingly, soft Ni(II) atoms turned out to have more strong bonds with hard base OH_2 molecule than with soft Py ligands.

In an attempt to get insight into the chemistry of the system under discussion and regularities of the ferromagnetic/antiferromagnetic complex interconversion, we studied the influence of organic base nature on the reaction course.
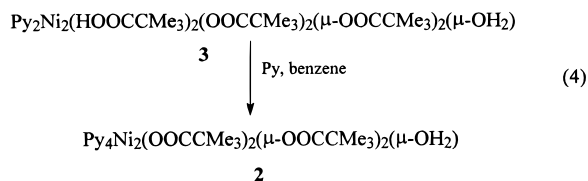
Binuclear Complexes. As it was mentioned above, the binuclear complex **2** containing four Py ligands undergoes transformation into the binuclear compound **3** containing two instead four molecules of basic ligand under heating at 100–140 °C in xylene or toluene solution[11] (eq 3). However the yield of complex **3** is far from quantitative one with maximum 50% of the initial **2** being transformed into complex **3**. This suggests byproduct formation to take place. We failed to identify the byproducts. Apparently, a mixture of related to complexes **2** and **3** is formed. In contrast to that, the treatment of the reaction mixture or the solution of pure complex **3** in benzene by 2 equiv of pyridine at 80 °C was shown to give rise to the practically quantitative formation of complex **2** (eq 4).

Thermolysis of solid **3** at 170 °C in vacuo results in the elimination of the two coordinated acid molecules and bridged

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(13) The detailed magnetic investigation of the freshly prepared single-crystal samples of the complexes described earlier as $L_4Ni_2(OOCCMe_3)_2$-$(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH)$ (L = Py, 3,4-Lut, Nic)[11] in the diapason 300–2 K showed that these compounds contain the Ni(II) atoms only and should be formulated as $L_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ (L = Py, 3,4-Lut, Nic).

Table 1. Main Geometric Parameters for Trimethylacetate Complexes $L_2Ni_2(OOCCMe_3)_4$ with China Lantern Structure
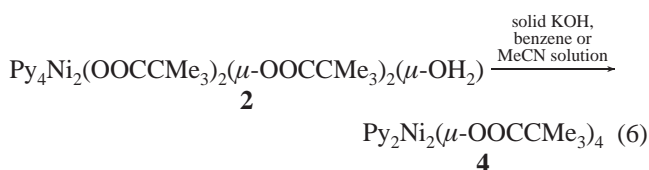
| NN	L	Ni···Ni, Å	Ni–N, Å	N–Ni···Ni, deg	ref
4	Py	2.603(2)	2.012(5)	176.8(2)	this work
5	2,3-Lut	2.726(2)	2.030(8)	168.3(1)	this work
	2,4-Lut	2.721(1)	2.032(4)	166.6(1)	10a
	2,5-Lut	2.7202(8)	2.034(3)	160.8(1)	10b
	2-methylquinoline	2.754(3)	2.047(9)	167.2(4)	7
	2-EtC_5H_4N	2.7227(7)	2.042(3)	166.00(6)	10b
	2-picoline	2.7171(7)	2.037(3)	169.47(7)	10b
6	Et$_3$N	2.728(2)	2.106(6)	177.7(3)	this work

$$Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$$

3

$$\Big\downarrow \text{Py, benzene} \qquad\qquad (4)$$

$$Py_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$$

2

water molecule. A binuclear complex $Py_2Ni_2(OOCCMe_3)_4$ (**4**) having the "chine lantern" structure was obtained as a product of the thermolysis (eq 5).

$$Py_2Ni_2(HOOCCMe_3)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$$

3

(5)

4
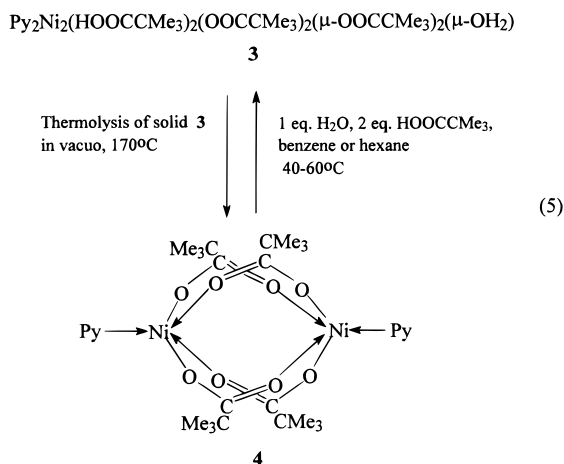
Complex **4** can also be prepared by the reaction of **2** with solid KOH in benzene or MeCN (eq 6).

$$Py_4Ni_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2) \xrightarrow[\text{MeCN solution}]{\text{solid KOH, benzene or}}$$
2

$$Py_2Ni_2(\mu\text{-}OOCCMe_3)_4 \quad (6)$$
4

Ultimately, a double-coordinated bridging H_2O molecule and two Py ligands were displaced out of the Ni(II) ion coordination sphere. Two terminal carboxylate ligands were converted into bridging groups in the reaction. To the best of our knowledge, this reaction is the only example of base nucleophilic substitution. Deprotonation of the bridging H_2O molecule seems to be the first step of the reaction (eq 7).

(7)

A
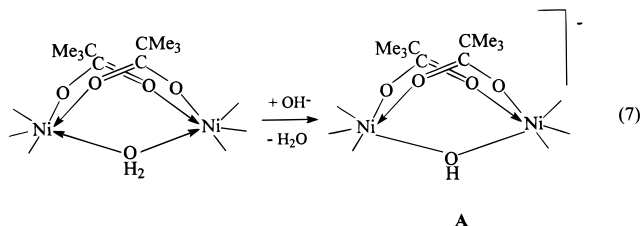
In the next step hydroxyde bridge of complex **A** is presumably splitted being attacked by another OH^- anion (eq 8).

Both OH^- ligands are substituted by the noncoordinated sites of terminal carboxylate ligands which are converted into bridging groups to give complex **4** as the final product. Surprisingly, the H_2O bridging group can be restored by reacting complex **4** with 1 equiv of H_2O and 2 equiv of $HOOCCMe_3$ in benzene or hexane solution at $40-60°$ as depicted by eq 5.

The X-ray analysis data (Table 1) show that the two Ni(II) atoms in **4** are bound together by four carboxylate groups (Ni–O $1.998(4)-2.003(4)$ Å). Each nickel atom is additionally bound

A

4 (8)
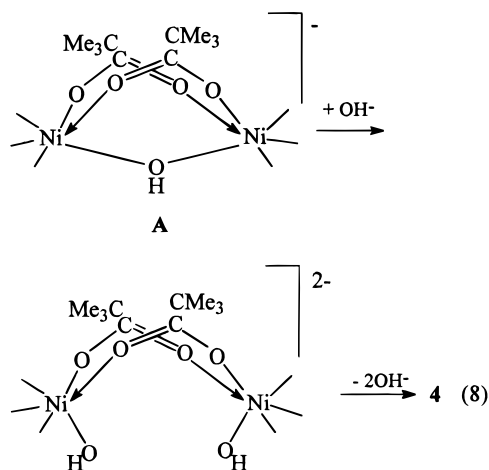
with the nitrogen atom of pyridine ligand. Fragment N–Ni··· Ni–N is close to be linear, the angle N–Ni···Ni being equal to $176.8(2)°$. The Ni···Ni separation in complex **4** is nonbonding though shortened in comparison with the observed for analogous dimers $L_2Ni_2(OOCCMe_3)_4$ containing α-substituted pyridines (L = 2-methylquinoline,[10b] 2,4-$Me_2C_5H_3N$,[10a] 2,5-$Me_2C_5H_3N$,[10b] 2-EtC_5H_4N,[10b] 2-picoline[7]) (Table 1). The dimers can be prepared directly by reacting of complex **1** with corresponding pyridine base. Enhanced donor ability of the ligands originated from alkyl group influence seem to favor the formation of this type of complexes. For example, the interaction of **1** and 2,3-lutidine at 60 °C affords tetracarboxylate complex (2,3-$Me_2C_5H_3N)_2Ni_2(OOCCMe_3)_4$ (**5**) in a good yield (eq 9).
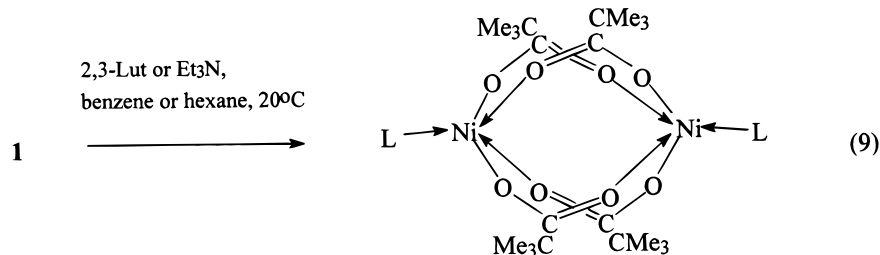
According to X-ray data the geometry of molecule **5** is similar to that of complex **4** (Table 1). However in this case the Ni···Ni distance $(2.726(2)$ Å) is noticeably longer, and the N–Ni···Ni moiety differs from linear more markedly $(168.3-(1)°)$ than that observed for the pyridine dimer **4**. Surprisingly, a complex similar to complex **5** was obtained in a good yield by reacting **1** with Et_3N. Three alkyl groups of this base produces substantial sterical hindrance in the nickel coordination sphere. The structure of the dinickel tetracarboxylate core in the complex $(Et_3N)_2Ni_2(OOCCMe_3)_4$ (**6**) (Figure 1, Table 1) is very close to that observed for complex **5** (Ni–O $2.004(5)-2.023(8)$ Å). Again, nonbonding Ni···Ni separation $(2.728(2)$ Å) and a nearly linear fragment N–Ni···Ni $(177.7(3)°)$ are seen in the structure of complex **6**. However the Ni–N distances in the complex are significantly longer than that one observed for complexes $L_2Ni_2(OOCCMe_3)_4$ (Table 1). The complexes **5** and **6** easily react at $40-60°$ with pyridine to give **4** in a practically quantitative yield (eq 10).

In this view complex **6** seems to be a good starting compound for the preparation of a number different nickel dimers with the china lantern structure. However, the reverse conversion of complex **4** into complex **6** was not observed.

Each Ni ion in complexes **4–6** and related compounds can be conventionally considered to have a distorted square-pyramidal environment with an N atom in apic position and four oxygen atoms in equatorial plane. The central Ni atom is placed above the oxygen atom plane being shifted toward the N-containing ligand. Within this scheme the N–ligand/Ni···Ni distance interrelation can be treated as an consequence of both trans-influence of the donor ability of the N base and steric hindrances (Table 1).

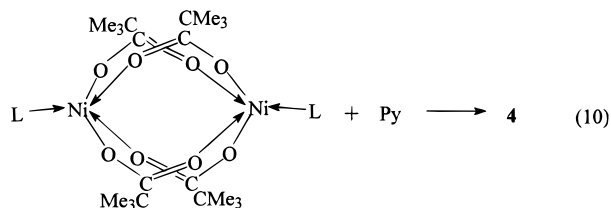Tetrabridged trimethylacetate dimers **4–6** display complicated magnetic behavior.

The effective magnetic moment of complexes **4** and **5** was found to decrease from 2.41 to 0.2 μB (for **4**) and from 3.16 to

$$
\mathbf{1} \quad \xrightarrow{\substack{\text{2,3-Lut or Et}_3\text{N,} \\ \text{benzene or hexane, 20}^{\circ}\text{C}}} \quad
$$

(9)

L = 2,3-Lut (**5**), Et₃N (**6**)

0.1 μB (for **5**) in the interval of $300-2$ K (Figures 2 and 3). Analogues trend to decrease μ values from 2.83 to 2.61 μB was observed for the triethylamine complex **6** in the temperature range of $300-77$ K. Since the magnetic behavior of dimers **4**–**6** is typical for the observed earlier dimeric tetracarboxylate complexes exhibiting antiferromagnetic exchange,[5,10a] the theoretical calculations by means of Heisenberg–Dirack–Van Vleck model[15] do not give adequate results. New theoretical approaches are more than likely required.

Complexes with 2,2′-Dipyridyl. 2,2′-Dipyridyl with its strong chelating effect is a well-known bidentate ligand capable of forming monomeric complexes with 3d elements. Reaction between cluster **1** and the stoichiometric amount of 2,2′-dipy at Ni(at):Dipy = 1:1 molar ratio affords binuclear complex Dipy₂Ni₂(OOCCMe₃)₂(μ-OOCCMe₃)₂(μ-OH₂) (**7**) in a high yield (60–70%) (Scheme 1).

$$
\text{L} \rightarrow \text{Ni} \qquad \text{Ni} \leftarrow \text{L} \quad + \text{ Py} \longrightarrow \mathbf{4} \qquad (10)
$$

L = 2,3-Lut (**5**), Et₃N (**6**)

According to X-ray data (Figure 4), the main geometric characteristics of the metal core of complex **7** are very close to those observed for complex **2** (Table 2). The difference between the structures **2** and **7** is the different orientations of the pairs of the six-membered pyridine cycles bound to Ni(II) atom. The almost planar dipyridyl ligand was found in complex **7** with the dihedral angle between C₅H₄N rings being equal to 3.2(2)°. Less pronounced Py ring planes folding is observed in complex **2** (angles between the planar pyridine ligands coordinated to Ni(II) atom are equal 104.2(3) and 101.6(3)°). As a consequence, the ligand environment of nickel atoms in complex **7** is distorted.

Magnetic behavior of the binuclear three-bridged complex **7** (Figures 5 and 6) considerably differs from **4**–**6**, and in this case the magnetic moment increases slowly with the temperature decrease achieving maximum at 10 K and then decreases. These variations of magnetic moment in temperature can imply a ferromagnetic interaction in the binuclear metal fragment ($g = 2.13$, $S_1 = S_2 = 1$, $J_1 = 2.0$ cm⁻¹) as well as weak intermolecular interaction (ZJ¹ = −0.15 cm⁻¹).

Unlike that of complexes **2** or **3**, the thermolysis of solid **7** at 170 °C gives monomeric complex DipyNi(OOCCMe₃)₂ (**8**) (Scheme 1) isolated after recrystallization as blue prisms. Mononuclear complex **9** was also obtained when complex **7** was treated with aniline (**7**:PhNH₂ = 1:2) in benzene solution at 20° (Scheme 1). Both complexes **8** and DipyNi(NH₂Ph)-

(OOCCMe₃)₂ (**9**), were characterized by X-ray data (Figures 7 and 8, Table 3). In both molecules **8** and **9**, the metal atoms have distorted octahedral ligand environment and 20-electron configuration. However, in complex **8**, the nickel atom is surrounded with two N atoms of the dipyridyl ligand and four oxygen atoms of the chelating carboxylate groups. In contrary to that, Ni(II) atom in complex **9** is connected with formally four different ligands including dipyridyl molecule, aniline molecule, monodentately coordinated terminal carboxylate group and chelating carboxylate group. Since the unit cells of **8** and **9** contain two independent molecules of the racemic mixture, the synthetic method of the preparation of the hetero-ligand complex **9** demonstrates a possible general approach for the chemical designing optically active magnetic complexes of Ni-(II) when complex **7** or its analogue will be used as a starting material.

Complex with Terpyridine. Terpyridine is a chelator containing three pyridine cycles and widely used as a strong chelating agent to extract heavy metals out of solution. In contrast to pyridine and dipyridyl, the one-step reaction of terpyridine with cluster **1** affords immediately monomeric complex TerpyNi(OOCCMe₃)₂ (**10**) (eq 11).

$$
\mathbf{1} \quad \xrightarrow{\text{Terpy, benzene or hexane, 20 }^{\circ}\text{C}} \quad
$$

(11)

10
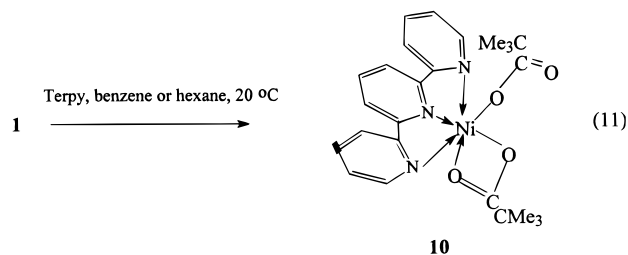
Complex **10** contains two different carboxylate groups similarly to complex **9**. One of them is monodentately coordinated as a terminal ligand, and the other one has a chelating coordination. The X-ray data (Figure 9, Table 3) show that planar terpyridine ligand uses all three nitrogen atoms to be bound to the Ni(II) atom. Three N atoms of Terpy ligand and one oxygen atom of the chelating trimethylacetate group form plane surrounding of Ni atom. The second oxygen atom of this chelating group and oxygen atom of the terminal carboxylate fragment are placed above and below the N₃NiO plane occupying apical positions of the octahedron. The O–Ni–O fragment is nonlinear (corresponding angle is equal to 155.8(2)°). As a result, Ni(II) atom in **10** with 20 electrons has a distorted

(14) For example, see: (a) Agnew, N. H.; Larkworthy, L. F.; Webb, A. G. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 303. (b) Patel, R. W.; Romana Rao, D. W. *Z. Anorg. Allg. Chem.* **1967**, *351*, 68. (c) Neiding A. B. *Magnetokhim. Itogi nauki Moskva* **1970**, 152 [*Magnetochemistry, Moscow* **1970**] (in Russian).

(15) Van Vleck, J. H. *The Theory of Electronic and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

Scheme 1
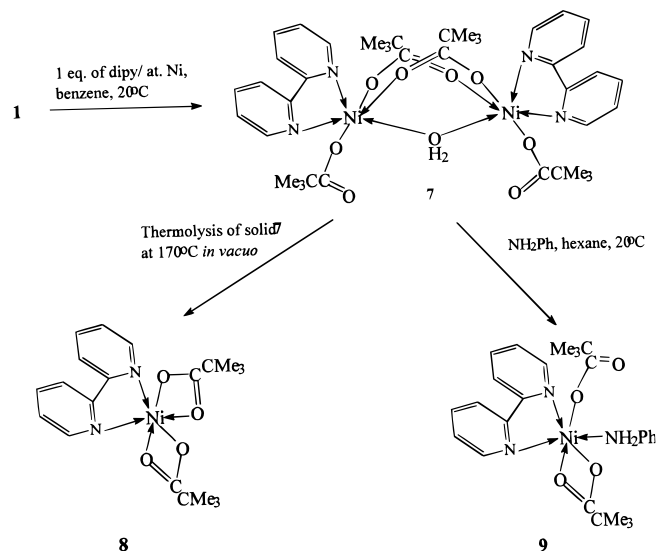
octahedral ligand environment. The effective magnetic moment of the monomers **8**−**10** is similar and independent of the temperature in the range of 300−77 K (3.09−3.12 μB). Such a behavior is typical for the Ni(II) ions with $S = 1$ and $g = 2.18$ for mononuclear compounds.[14]
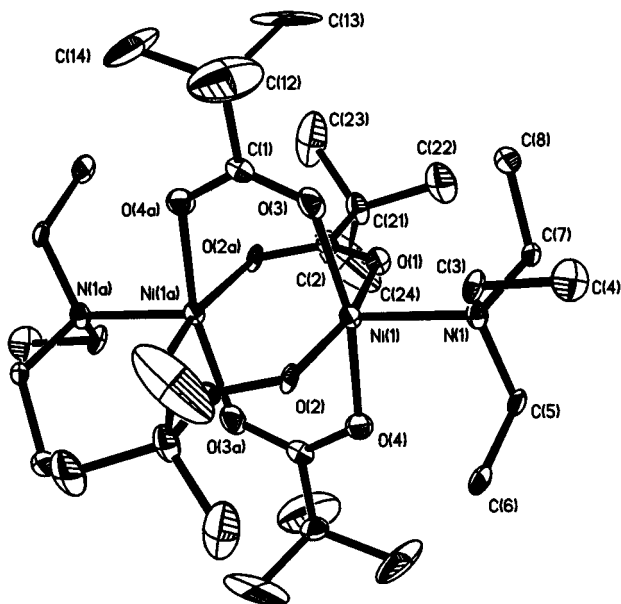
Figure 1. Molecular structure of $(Et_3N)_2Ni_2(OOCCMe_3)_4$ (**6**).
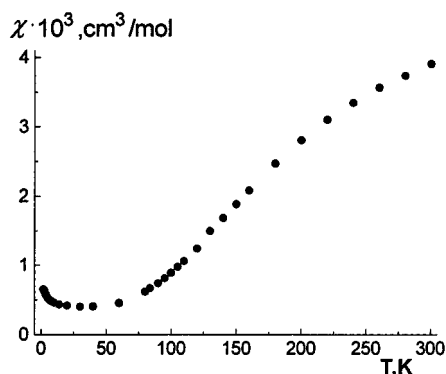
Figure 2. Magnetic susceptibility vs temperature plot for complex **5** ($\chi_d = -426.46 \times 10^{-6}$ cm^3/mol).
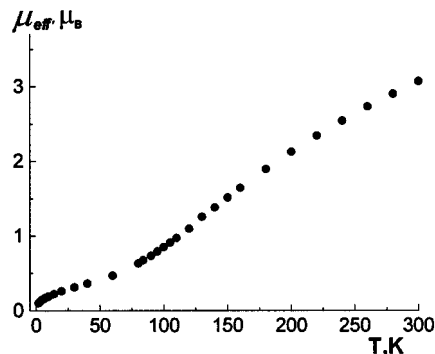
Figure 3. The temperature dependence of magnetic moment for complex **5**.

Conclusions

The scope of reactions observed between the complex **1** pyridine ligands L is depicted by Scheme 1. It is easily seen that the product nuclearity of a reaction administrated by the ligand dentaty. The degree of the degradation of the nine-nuclear metal core of initial complex **1** is regulated by the number of pyridine cycles of ligand L. Thus, the binuclear species **2**, **3**, and **7** are the main products of the interaction of complex **1** with ligands that have one or two cycles (Py or Dipy). However, if the number of cycles is equal to 3 (terpyridine), the monomeric complex **10** is formed. The reaction conditions play also rather important role and can be a regulating factor to determine the structure type of the products formed. Equations 2−6 illustrate this transformations of the pyridine-containing complexes when the binuclear three-bridged complexes with the 20-electron Ni-(II) atoms **2** and **3** undergo transformations to the 18-electron Ni(II) tetra-bridged carboxylate compound **4** under thermolysis. In a similar situation the dipyridyl ligand in the binuclear complex **7** cannot be split with the formation of monopyridine fragment as it was observed upon the thermolysis of **2** in solution. By this reason complex **7** is more stable in organic solution (20−140°) but reacts giving rise the monomer **8** under more drastic conditions in the solid state. Finally, the mono-merization process is stimulated by the insertion in reaction media of aniline ligand leading to the formation of asymmetric complex **9** (see Scheme 1).

The ability of water molecule to serve as a group bridging two Ni(II) ions seems to be both unexpected and remarkable phenomenon. The H_2O bridge have been proven to be resistant to the action of thermolysis (eqs 2 and 3) and strong nucleo-philes. Only a hard nucleophilic agent as strong as OH$^-$ ion was found to be capable of splitting the bridge Ni(H$_2$O)Ni probably via intermediate Ni(OH$^-$)Ni group formation.

A quantitative agreement between Ni···Ni distances observed for H_2O-bridged structures (Table 2) and that one found for Ni urease[2] (3.5 Å) is worthy of notice. The coincidence of the distances suggests possible similarities in the observed structures of Ni(H$_2$O)Ni complexes and Ni···Ni sites in Ni-urease. This brings up the question: What is the detailed structure of urease metal site?

Experimental Section

General Comments. All operations including the synthesis of the complexes were carried out under an atmosphere of dry oxygen-free argon using standard Schlenk techniques. THF, Et$_2$O, benzene, toluene, and xylene were purified by distillation from sodium/benzophenone ketyl. Pentane, hexane, and heptane were dried by boiling over sodium. Dichloromethane (CH$_2$Cl$_2$) and MeCN were distilled twice from P$_2$O$_5$. The starting materials Ni$_9$(HOOCCMe$_3$)$_4$(μ_4-OH)$_3$(μ_3-OH)$_3$(OOCCMe$_3$)$_{12}$
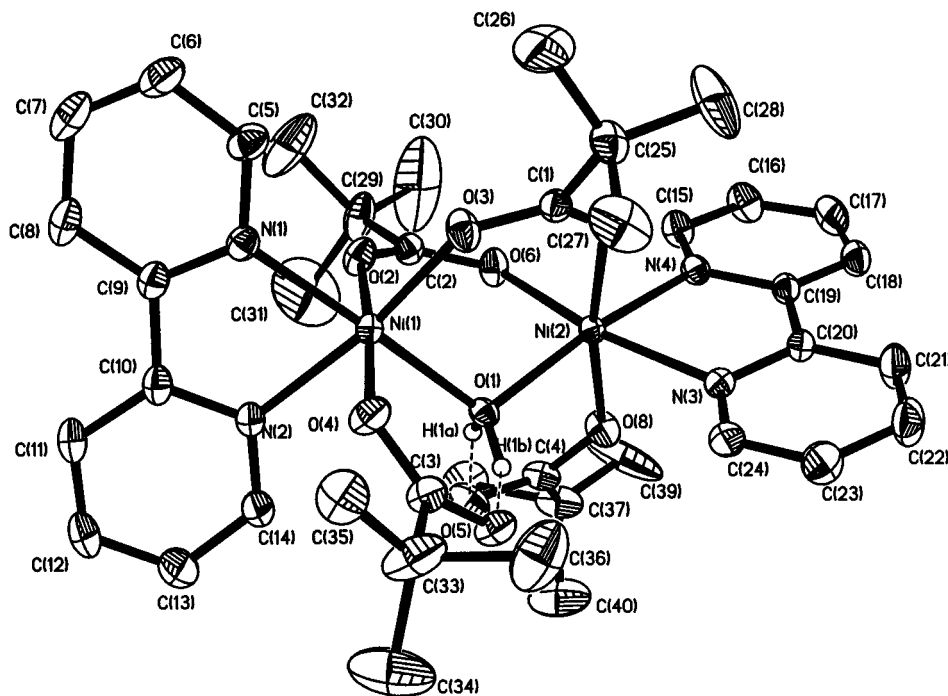
Figure 4. Perspective view of the molecular structure of (Dipy)$_2$Ni$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**7**) (one from two independent molecules).

(**1**), Py$_4$Ni$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**2**), and Py$_2$Ni$_2$-(HOOCCMe$_3$)$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**3**) were prepared as described elsewhere.[11] Infrared spectra were obtained from a Specord M82 spectrometer in KBr pellets. The temperature dependence of the magnetic susceptibilities (χ_m) was determined by Faraday technique in the temperature range 296–77 K (for **4**, **6**, and **8**–**10**) or from SQUID-magnetometer MPMS-5S Quantium Design in the temperature range of 300–2 K (for **2**, **5**, and **7**). Details of the calculation of the magnetic moment ($\mu_{eff} = (8\chi_cT)^{0.5}$) and of the exchange parameters ($-2J$) by means of the HDVV model[14] ($H = -2J_{ij}S_iS_j$) were described earlier.[16]

Reaction of 3 with Pyridine. A green solution of Py$_2$Ni$_2$-(HOOCCMe$_3$)$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**3**) (451 mg, 0.5 mmol) and pyridine (0.70 mL, 1.1 mmol) in 30 mL of benzene was stirred at 20–60 °C for 0.5–1 h. A deep-blue solution formed was concentrated to 15 mL and cooled to 5–7 °C. The blue prisms of Py$_4$-Ni$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**2**) (351 mg, 0.41 mmol, 82%) that precipitated were separated from mother liquor, washed with cooled pentane (−10 °C), and dried in vacuo. The IR spectra and crystallographic data for the complex prepared were identical to those published.[11]

Reaction of 2 with Solid KOH. A blue solution of **2** (428 mg, 0.5 mmol) in 50 mL of MeCN (or in 60 mL of benzene) and 2 g of solid KOH were stirred at 50–70 °C for 1 h during which time the color changed to green-brown. The solvent was then evaporated in vacuo to dryness at 40–50 °C. The resulting green-brown powder was extracted with benzene, hexane, or heptane (60 mL). A green-brown extract was prepared which gave after cooling up to −10 °C green prisms of Py$_2$-Ni$_2$(OOCCMe$_3$)$_4$ (**4**) (251 mg, 0.37 mmol, 74%). Anal. Calcd for C$_{30}$H$_{46}$N$_2$Ni$_2$O$_8$: C, 52.99; H, 6.77; N, 4.12 Found: C, 52.5; H, 6.4; N, 3.9. IR (ν, cm^{-1}) (KBr pellet): 3086 w, 2963 s, 2932 m, 2876 m, 1616 v.s, 1493 s, 1462 m, 1431 s, 1382 s, 1363 s, 1271 w, 1234 v.s, 1153 w, 1104 m, 1073 s, 1042 s, 943 w, 900 m, 882 m, 801 s, 764 s, 703 vs, 635 s, 443s. The green prisms of **4**·2CH$_2$Cl$_2$ which were suitable for an X-ray study were obtained by slow cooling of a hot solution of a mixture of CH$_2$Cl$_2$/heptane (1:1).

Thermolysis of 3. Solid **3** (451 mg, 0.5 mmol) was heated to 170 °C in vacuo for 1.5 h. The green-brown solid was extracted by benzene or toluene (40–50 mL). This extract gave green crystals of **4** (299 mg, 0.44 mmol, 88%) after concentration to 15 mL and cooling (5–0 °C).

Reaction of 4 with Water and Pivalic Acid. A reaction mixture of **4** (340 mg, 0.5 mmol), water (0.1 mL, 0.56 mmol) and HOOCCMe$_3$ (1 mL, 1.23 mmol) in 40 mL of toluene was refluxed for 1.5–2 h. The

resulting solution was concentrated to 10 mL. Cooling of this concentrate to −10 °C yielded green prisms of **3** (352 mg, 0.39 mmol, 78%).

Reaction of 2,3-Lutidine and Et$_3$N with 1. A bright green solution of Ni$_9$(HOOCCMe$_3$)$_4$(μ_4-OH)$_3$(μ_3-OH)$_3$ (OOCCMe$_3$)$_{12}$ (**1**) (2250.3 mg, 1 mmol) and 9 mmol of lutidine or 12 mmol of Et$_3$N in 70 mL of hexane was refluxed for 1 h. The solvent was removed to dryness. The resulting greenish solid was extracted by hexane or heptane. This extracts gave green plates of L$_2$Ni$_2$(OOCCMe$_3$)$_4$ (L = 2,3-Lut (**5**), Et$_3$N (**6**)) after cooling to −10 °C. Yield of **5**: 625 mg, 0.85 mmol, 85%. Yield of **6**: 441 mg, 0.61 mmol, 61%. Anal. Calcd for C$_{34}$H$_{54}$N$_2$Ni$_2$O$_8$ (**5**): C, 55.48; H, 7.34; N, 3.81. Found: C, 55.2; H, 7.4; N, 3.6. IR (ν, cm^{-1}) (KBr pellet): 3098 w, 2963 c, 2932 m, 2870 m, 1623 v.s, 1493 s, 1462 w, 1431 vs, 1382 s, 1376 m, 1363 m, 1295 m, 1264 w, 1234 s, 1203 s, 1098 m, 1024 m, 900 m, 801 m, 764 w, 733 w, 684 w, 635 s, 443 s. Anal. Calcd for C$_{32}$H$_{66}$N$_2$Ni$_2$O$_8$ (**6**): C, 52.43; H, 9.01; N, 3.82. Found: C, 52.5; H, 8.9; N, 3.9. IR (ν, cm^{-1}) (KBr pellet): 2953 s, 2934 m, 2900 m, 2874 m, 2849 m, 1624 s, 1480 s, 1462 m, 1452 m, 1424 s, 1374s, 1360 s, 1228 s, 1176 m, 1152 m, 1106 m, 1084 m, 1032 m, 1006 m, 914 m, 892 s, 844 m, 815 m, 798 s, 788 m, 774 m, 740 s, 615 s, 556 s, 507 m, 470 m.

Reaction of 5 and 6 with Pyridine. A green solution of **5** (368 mg, 0.5 mmol) or **6** (362 mg, 0.5 mmol) and pyridine (0.70 mL, 1.1 mmol) in benzene (40 mL) was stirred at 60–80 °C (for **6** at 20–40 °C) for 1 h. The resulting mixture was concentrated to 15 mL. Cooling of this extract to 5 °C afforded green prismatic crystals of **4**. Yield: 211 mg, 0.31 mmol, 62% (in the case of **5** as initial compound); 312 mg, 0.46 mmol, 92% (in the case of **6** as initial compound).

Reaction of 1 with Dipy. A bright green solution of **1** (1125 mg, 0.5 mmol) and dipyridyl (702 mg, 4.5 mmol) in benzene (50 mL) was refluxed for 1 h during which time the color changed to green-blue. The solvent was removed in vacuo to dryness. A green precipitate was extracted with a mixture benzene/heptane (1:2, 100 mL), and a green-blue solution formed, which was concentrated to 35 mL at 45 °C/0.1 Torr. This extract gave green prismatic crystals of Dipy$_2$Ni$_2$(OOCCMe$_3$)$_2$-(μ-OOCCMe$_3$)$_2$(μ-OH$_2$) (**7**) (272 mg, 0.32 mmol, 64%) after cooling to 5–7 °C. Anal. Calcd for C$_{40}$H$_{54}$N$_4$Ni$_2$O$_9$: C, 56.38; H, 6.34; N, 6.58. Found: C, 56.5; H, 6.2; N, 6.7. IR (ν, cm^{-1}) (KBr pellet): 3111 m,

(16) Rakitin, Yu. V.; Kalinnikov, V. T. *Sovremennaya magnetokhimiya* Nauka: St-Peterburg, 1994 (in Russian) [*Modern magnetochemistry*; Science: St. Peterburg, 1994].

Table 2. Main Geometric Parameters for Binuclear Trimethylacetate Complexes L$_2$L'$_2$Ni$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)$_2$(μ-OH$_2$)

NN	L and L'	Ni···Ni, Å	Ni–O (OOCR$_{bridge}$), Å	Ni–O (OOCR$_{terminal}$), Å	Ni–N, Å	Ni–O (μ-OH$_2$), Å	Ni–O–Ni, deg	ref
2	L = L' = Py	3.513(1)	2.012(2)–2.037(2)	2.056(2)	2.104(3)–2.123(4)	2.074(2); 2.078(3)	115.6(1)	11
	L = L' = 3,5-Lut	3.549(3)	1.989(8)–2.023(9)	2.099(3)	2.088(12)–2.103(9)	2.104(6)	114.9(2)	11
	L = L' = Nic	3.505(4)	1.999(12)–2.030(11)	2.018(12)–2.062(13)	2.125(15)–2.155(13)	2.077(12); 2.091(11)	114.4(5)	11
3	L = Py, L' = HOOCCMe$_3$	3.465(2)	1.983(5)–1.992(5)	2.069(5)	2.097(7) 2.142(5)^b	2.106(4)	110.7(3)	11
7	LL' = Dipy^a	3.479(1)	2.009(3)–2.040(3)	2.043(3); 2.063(4)	2.056(3)–2.114(3)	2.092(3); 2.079(3)	113.0(1)	this work
		3.488(1)	2.011(4)–2.070(3)	2.052(3); 2.039(3)	2.059(3)–2.109(3)	2.089(3); 2.079(3)	113.6(1)	

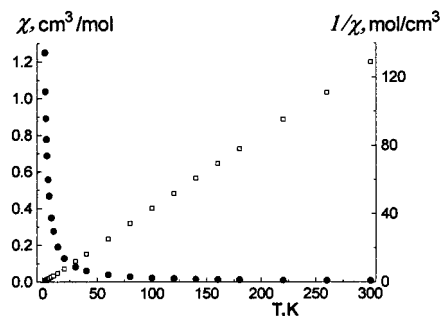^{a} Two independent molecules in unit cell. ^{b} Ni–O(HOOCCMe$_3$).

Figure 5. Magnetic susceptibility and $1/\chi$ function vs temperature for complex **7** ($\chi_d = -488.01 \times 10^{-6}$ cm^3/mol).
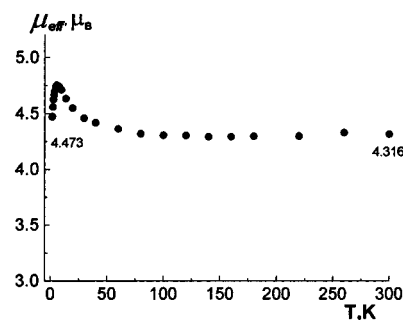

Figure 6. The temperature dependence of effective magnetic moment for **7**.

3055 m, 3031 m, 2950 s, 2962 m, 2876 m, 1604 vs, 1530 m, 1481 m, 1546 m, 1456 m, 1425 m, 1363 m, 1320 m, 1234 s, 1166 m, 1122 w, 1055 w, 1024 s, 882 s, 770 v.s, 746 m, 667 m, 616 vs, 530 m, 425 s.

Formation of DipyNi(OOCCMe$_3$)$_2$ (8). A solid complex **7** (425 mg, 0.5 mmol) was heated to 170 °C in vacuo for 1.5 h. The blue-violet solid was extracted with a mixture benzene/heptane (40−50 mL). This extract gave deep blue crystals of **8** (333 mg, 0.80 mmol, 80%) after concentration to 15 mL and cooling (5−0 °C). Anal. Calcd for C$_{20}$H$_{26}$N$_2$NiO$_4$: C, 57.60; H, 6.24; N, 6.72. Found: C, 57.5; H, 6.0; N, 6.4. IR (ν, cm^{-1}) (KBr pellet): 3077 m, 3047 m, 2934 s, 2895 m, 2840 m, 1601 vs, 1569 m, 1520 s, 1482 s, 1442 s, 1430 s, 1410 s, 1377 m, 1356 s, 1312 s, 1224 s, 1142 s, 1092 m, 1060 m, 1048 m, 1018 s, 898 s, 874 s, 810 m, 776 s, 736 m, 652 s, 636 s, 608 s. The crystals of **8**·0.5MeCN which were suitable for an X-ray study were obtained by slow cooling of a hot solution of **8** in MeCN to room temperature.

Formation of DipyNi(PhNH$_2$)(OOCCMe$_3$)$_2$ (9). A green solution of **7** (425 mg, 0.5 mmol) and aniline (1.5 mL, 2.02 mmol) in benzene (50 mL) was refluxed for 1 h during which time the color changed to blue. The resulting mixture was concentrated to 15 mL. Cooling of this concentrate to 5 °C afforded green-blue prismatic crystals of solvate DipyNi(PhNH$_2$)(OOCCMe$_3$)$_2$·0.5PhNH$_2$·0.25C$_6$H$_6$ (**9**·0.5PhNH$_2$·0.25C$_6$H$_6$) (415 mg, 0.72 mmol, 72%) suitable for an X-ray investigation. Anal. Calcd for C$_{26}$H$_{33}$N$_3$NiO$_4$·PhNH$_2$·0.5C$_6$H$_6$: C, 65.45; H, 6.70; N, 8.73. Found: C, 65.2; H, 6.4; N, 8.9. IR (ν, cm^{-1}) (KBr pellet): 3284 m, 3253 m, 3129 m, 3086 m, 3043 m, 2956 s, 2926 m, 2864 m, 1610 vs, 1573 vs, 1542 s, 1493 s, 1450 s, 1413 s, 1366 s, 1320 m, 1234 s, 1160 m, 1061 s, 1024 m, 894 m, 801 m, 770 s, 746 s, 703 s, 670 m, 635 m, 616 m, 567 w, 542 w, 425 m.

Formation of TerpyNi(OOCCMe$_3$)$_2$ (10). A bright green solution of **1** (675 mg, 0.3 mmol) and terpyridyle (700 mg, 3 mmol) in benzene (80 mL) was refluxed for 1 h during which time the color changed to brown-green. The solvent was removed in vacuo to dryness. A brown precipitate was extracted with MeCN (50 mL), and a brown-green solution formed, which was concentrated to 20 mL at 50 °C/0.1 Torr. This extract gave green-brown prismatic crystals of solvate TerpyNi-(OOCCMe$_3$)$_2$·MeCN (**10**·MeCN) (898 mg, 1.68 mmol, 62%) after cooling to −10 °C. Anal. Calcd for C$_{25}$H$_{29}$N$_3$NiO$_4$·MeCN: C, 60.59; H, 5.98; N, 10.47. Found: C, 61.1; H, 5.9; N, 10.6. IR (ν, cm^{-1}) (KBr pellet): 3142 w, 3092 w, 2997 s, 2984 s, 2948 m, 2891 m, 1611 vs, 1563 vs, 1512 s, 1481 w, 1461 s, 1444 s, 1410 m, 1392 m, 1351 w,

Table 3. Main Geometric Parameters for Mononuclear Trimethylacetate Ni(II) Complexes with 2,2′-Dipyridyl and Terpyridine

compound	Ni–N, Å	Ni–O ($OOCR_{terminal}$), Å	Ni–O ($OOCR_{chelate}$), Å
DipyNi(OOCCMe$_3$)$_2$ (**8**)[a]	2.033(3); 2.059(4)		2.106(4); 2.137(3)
	2.037(3); 2.052(5)		2.104(4); 2.135(4)
DipyNi(NH$_2$Ph)(OOCCMe$_3$)$_2$ (**9**)[a]	Dipy:	2.039(4)	2.059(5); 2.194(4)
	2.066(6); 2.075(5)	2.039(4)	2.059(5); 2.194(4)
	2.053(6); 2.073(5)	2.023(4)	2.070(5); 2.221(4)
	NH$_2$Ph:		
	2.097(4)		
	2.113(4)		
TerpyNi(OOCCMe$_3$)$_2$ (**10**)	2.087(4)	1.994(3)	2.073(4); 2.176(2)
	1.991(4); 2.113(3)		

[a] Two independent molecules in unit cell.
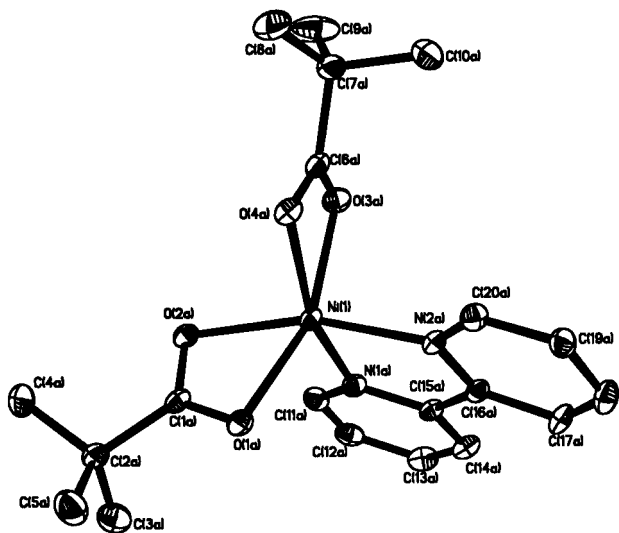
Figure 7. Molecular structure of DipyNi(OOCCMe$_3$)$_2$ (**8**).
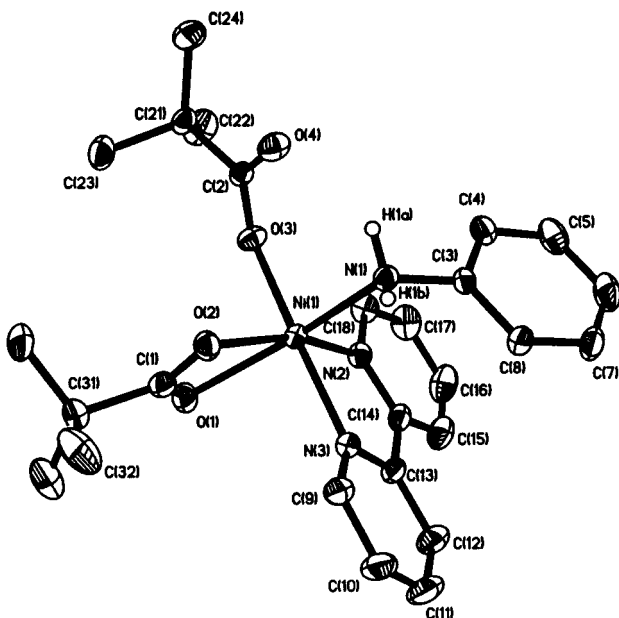
Figure 8. Molecular structure of (Dipy)(PhNH$_2$)Ni(OOCCMe$_3$)$_2$ (**9**).

1251 m, 1215 w, 1192 w, 1122 w, 1042 m, 901 m, 810 m, 782 s, 742 w, 652 m, 632 m, 609 m, 530 w, 423 m.

Crystal Structure Determinations. Single crystals of **4**–**10** for X-ray studies were obtained as described above. The samples were all mounted in air on glass fibers using 5-min epoxy resin. The unit cells were determined and refined from 24 equivalent reflections with $2\theta <$ 24–28° and obtained from Siemens R3/PC (for **4**, $T = 22$ °C; **6**, $T =$ 22 °C; **8**, $T = -100$ °C; and **9**, $T = 22$ °C) or CAD-4 (for **5**, **7**, and **10**,
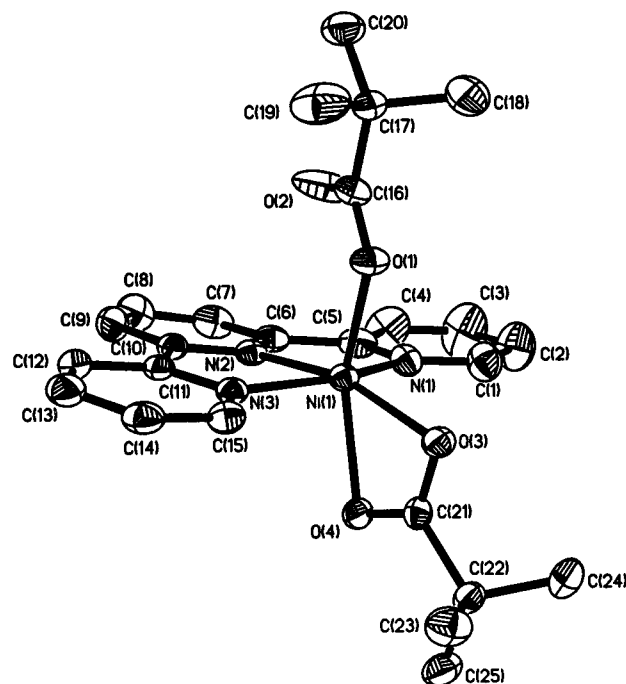
Figure 9. Molecular structure of TerpyNi(OOCCMe$_3$)$_2$ (**11**).

$T = 22$ °C) four-circle diffractometers (graphite monochromator, Mo Kα, $\lambda = 0.710\ 73$ Å). The intensity data sets were corrected for Lorenz and polarization effects. Backgrounds were scanned for 25% (for Siemens) or for 12.5% (for CAD-4) of the peak widths on each end of a scan. Three reflections were monitored periodically for each compound as a check for crystal decomposition or movement. No significant variation in these standards was observed; therefore, no correction was applied. The absorption correction was not used due to low coefficient for all of the complexes (Table 4). Details of crystal parameters, data collection, and structure refinement are given in Table 4.

All structures were solved using direct methods to locate the Ni atoms and most O, N, and C atoms. Standard Fourier methods were used to locate the remaining non-hydrogen atoms in molecules. An anisotropic refinement was applied to all non-hydrogen atoms. The H atoms of the pyridine rings, Et$_3$N, Ph, and CMe$_3$ groups were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.08$ Å^2. The H atoms of the bridged water molecule in **7** and of the NH$_2$ fragment of aniline in **9** were taken from a difference Fourier map and refined isotropically. Computations were performed using the SHELXTL PLUS program package[17] on a Pentium 166 computer. The function minimized in the least-squares calculations was $\Sigma w(F_o - F_c)^2$. Selected bond lengths and angles for investigated compounds are given in Tables 1–3. Additional information is available as Supporting Information.

(17) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases;* Clarendon Press: New York, 1985; p 175.

Table 4. Data Collection and Processing Parameters for Investigated Compounds

compound	4·2CH$_2$Cl$_2$	5	6	7	8·0.5MeCN	9·0.5H$_2$NPh·0.25C$_6$H$_6$	10·MeCN
formula	C$_{30}$H$_{46}$N$_2$Ni$_2$O$_8$·2CH$_2$Cl$_2$	C$_{34}$H$_{54}$N$_2$Ni$_2$O$_8$	C$_{32}$H$_{66}$N$_2$Ni$_2$O$_8$	C$_{40}$H$_{54}$N$_4$Ni$_2$O$_9$	C$_{20}$H$_{26}$N$_2$NiO$_4$·0.5MeCN	C$_{25}$H$_{33}$N$_3$NiO$_4$·0.5H$_2$NPh·0.25C$_6$H$_6$	C$_{25}$H$_{29}$N$_3$NiO$_4$·MeCN
mol wt	850.2	736.4	724.2	852.6	437.7	570	535.3
color and habit	green prism	green prism	green prism	green-blue prism	blue prism	green-blue prism	brown-green prism
space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1$	P-1	P-1	$P2_1/n$
a (Å)	10.756(6)	9.629(2)	10.197(3)	11.753(2)	11.456(2)	13.407(6)	15.744(3)
b (Å)	13.003(6)	10.860(2)	17.558(4)	21.631(4)	12.916(3)	15.069(6)	12.656(2)
c (Å)	15.273(7)	111.188(2)	12.004(3)	17.663(4)	17.687(4)	17.546(7)	15.875(3)
α (deg)	90	61.35(3)	90	90	83.02(3)	114.30(3)	90
β (deg)	93.19(4)	71.90(3)	112.37(2)	90.19(3)	74.63(3)	98.96(3)	118.78(3)
γ (deg)	90	82.65(3)	90	90	69.71(3)	103.14(3)	90
V (Å^3)	2133(2)	975.7(3)	1987.4(9)	4490.3(16)	2365.6(12)	3019(2)	2772.5(10)
Z	2^a	1^a	2^a	4^b	2^b	2^b	4
d$_{calcd}$ (g cm^{-3})	1.368	1.284	1.210	1.259	1.229	1.248	1.282
abs coeff (cm^{-1})	11.79	10.12	9.91	8.91	8.47	6.80	7.37
scan type	θ−2θ	κ−2θ	θ−2θ	κ−2θ	θ−2θ	θ−2θ	k−2θ
scan speed	variable, 2.51−14.65	variable, 2.51−14.65	variable, 2.51−14.65	variable, 2.02−29.30	variable, 2.02−14.65	variable, 2.54−14.65	variable, 2.50−29.60
scan width (deg)	1.80	1.80	1.80	1.80	1.40	2.00	1.80
2θ range (deg)	3−55	2−54	2−50	2−60	3−50	2−54	3−52
unique data	5140	3438	1841	11092	6054	10651	4128
reflns obsd	2651	3056	1236	8989	4272	7720	3164
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F) + 0.1090F^2$	$w^{-1} = \sigma^2(F) + 0.0116F^2$	$w^{-1} = \sigma^2(F) + 0.0029F^2$	$w^{-1} = \sigma^2(F) + 0.0049F^2$	$w^{-1} = \sigma^2(F) + 0.0039F^2$	$w^{-1} = \sigma^2(F) + 0.0147F^2$
GOF	1.55	0.43	0.66	0.98	0.82	1.52	0.68
R	0.064	0.084	0.054	0.040	0.049	0.075	0.047
R_w	0.068	0.088	0.073	0.0059	0.065	0.081	0.053
residual extrema in final diff map (e Å^{-3})	0.47 to −0.55	1.32 to −1.27	0.52 to −0.47	0.49 to −0.50	0.52 to −0.66	1.40 to −1.30	0.52 to −0.37

^{a} Molecules are placed in crystallographic center.

^{b} Two independent molecules in unit cell.

Specific Comments on the Solution and Refinements of 4, 5, and 7. All of these molecules show disordering of the CMe$_3$ fragments. The positions of these substituents were solved, and refinement of the population parameter resulted in a value close to 0.5. The disordering of the solvate CH$_2$Cl$_2$ molecule in the structure of **4**·2CH$_2$Cl$_2$ is observed. Both positions of dichloromethane were found and refined with the population factor of 0.5.

Supporting Information Available: Full tables of data collection parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen atoms coordinates and U values for **4−10**, and figures of complexes **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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