

Reviews

Trimethylacetate nickel complexes

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The present review is devoted to the chemistry of trimethylacetate Ni^{II} complexes with various nitrogen-containing ligands. Pathways of formation of complexes containing the $\text{Ni}_2(\mu\text{-OH}_2)(\mu\text{-OCCMe}_3)_2$ and $\text{Ni}_2(\mu\text{-OCCMe}_3)_4$ fragments are discussed. Pathways of degradation of the nine-nuclear complex $\text{Ni}_9(\text{HOCCMe}_3)_4(\mu_4\text{-OH})_3(\mu_3\text{-OH})_3(\mu_2\text{-OCCMe}_3)_{12}$ under the action of primary amines (aniline or propargylamine) as well as the process of dehydration of *N*-phenyl-*o*-phenylenediamine up to the bischelatate mononuclear complex $[1,2\text{-(NH)(NPh)C}_6\text{H}_4]_2\text{Ni}$ are demonstrated.

Key words: nickel(II) complexes, trimethylacetates, synthesis, structure, magnetic properties.

In recent years, carboxylate complexes of transition metals have attracted considerable attention of chemists primarily due to a wide diversity of their structures.^{1–5} The metal fragments of these complexes are often very similar to those present in metal-containing enzymes. Synthetic approaches, which have been developed by researchers involved in coordination and inorganic chemistry, can be successfully used for designing polyfunctional catalysts, which are analogs of natural enzymes. However, attempts to virtually completely reproduce metal fragments observed in enzymes^{6–11} including not only the nearest ligand environment but also the peripheral environment of particular metal centers are not necessarily successful due to the complexity of assembly of molecules whose protein residues, on the one hand, play an important role in electron transport and, on the other hand, are responsible for the geometric parameters of a mono-, bi-, or polynuclear fragment, which acts as an "engine" of this complex "biochemical machine." In our opinion, partial account of steric factors can be taken using a carboxylate anion containing a bulky strong

electron-donor substituent as a ligand directly bonded to the metal atom(s). Progress in "assembly" of such models depends to a large extent on advances in inorganic chemistry and the ability of chemists to synthesize transition-metal complexes whose metal fragments have geometric and electronic characteristics similar to those observed for the metal sites of the corresponding enzymes. This rather complicated problem calls for the development of synthetic methods as well as for detailed physicochemical studies of the structures, properties, and reactivity of new compounds. The severity of the problem stems from the fact that molecules that possess characteristics seemingly required for the realization of the catalytic process must withstand a medium in which the catalytic reaction proceeds, reagents that are "prepared" for interactions, *etc.* In spite of various limitations and difficulties associated with modeling of active moieties of metalloenzymes, the synthesis of model complexes is undoubtedly the first necessary step of attack on the problem of the design of artificial analogs of metal-containing enzymes.

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Since the magnetic and optical properties of complex carboxylates can be varied over a wide range as a function of their molecular structures, these complexes attract the attention not only of chemists but also of physicists. The carboxylate ligand can be readily eliminated upon thermolysis of the complexes. In addition, compounds of this class are volatile because their molecules are held in crystals through rather weak interactions. Owing to these facts complex carboxylates show considerable promise as starting compounds for preparing inorganic materials (primarily, oxides as films and finely dispersed compounds) that often possess unique electronic characteristics.

We used trimethylacetates (pivalates) of transition metals (in particular, of nickel) in investigations, which are the subject of the present review. Due to the presence of the bulky donor *tert*-butyl substituent possessing pronounced lipophilicity, transition-metal trimethylacetates are generally readily soluble in usual organic solvents, which is helpful in using these compounds in the synthesis as well as in studying their chemical properties. In this work, we discuss ways for controlling the assembly of nickel complexes with different numbers of nuclei (from the nine-nuclear to mononuclear complexes). Before we started our investigations in this field, only several structurally characterized nickel compounds with trimethylacetate ligands have been reported in the literature. Most of them belong to Ni^{II} dimers with the "China-lantern" structure and contain four bridging trimethylacetate groups that link two LNi fragments (L is an α -substituted pyridine ligand).¹²⁻¹⁴

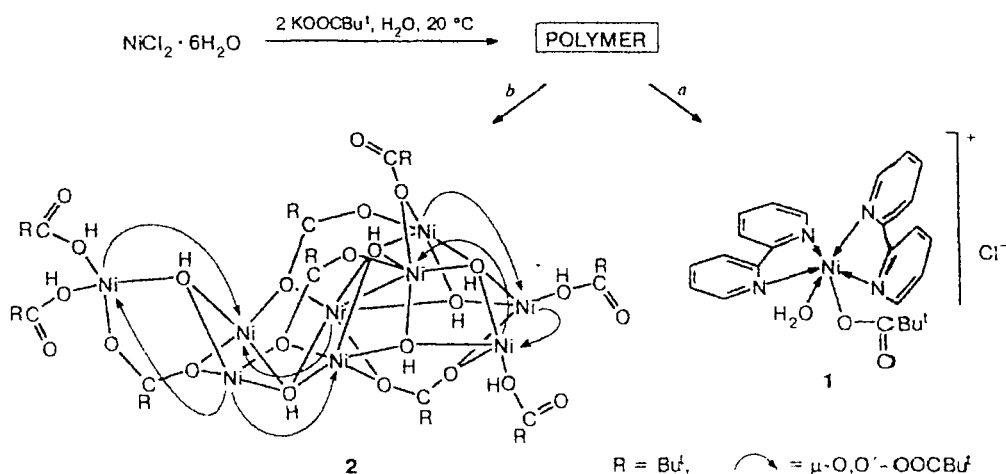
Synthesis and the structure of the starting nine-nuclear trimethylacetate nickel complex

The starting Ni^{II} compound containing trimethylacetate groups was synthesized by the exchange reaction

of NiCl₂ · 6H₂O with KOCCMe₃ (or with a mixture of KOH and HOCCMe₃) in water (the reagent ratio was 1 : 2).¹⁵ A coagulated pale-green water-insoluble precipitate was apparently a polymer and contained a small amount of unconsumed chloride ions. Treatment of this product with an excess of α,α -dipyridyl (dipy) in MeCN (Scheme 1, reaction *a*) afforded an insignificant amount (<2%) of the complex [dipy₂Ni(OH₂)(OCCMe₃)]Cl (**1**) (Ni—N, 2.047(3)—2.091(3) Å; Ni—O(OCCMe₃), 2.059(4) and 2.062(3) Å; Ni—O(OH₂), 2.074(4) and 2.102(3) Å; two independent molecules per asymmetric unit). However, after extraction of the above-mentioned polymer with nonpolar solvents (benzene, heptane, or hexane) (Scheme 1, reaction *b*), the nine-nuclear complex Ni₉(HOCCMe₃)₄(μ_4 -OH)(μ_3 -OH)(μ_n -OCCMe₃)₁₂ (**2**) was isolated in high yield (70–90%).¹⁵

According to the data of chemical analysis, cluster **2** contains 1.80 carboxylate groups (in the protonated or deprotonated form) and approximately 0.65 oxygen atoms (apparently as hydroxy groups) per nickel atom. The structures of compounds of this type have not been studied previously. X-ray diffraction analysis of very unstable crystals of **2**¹⁵ demonstrated that this compound is a nine-nuclear cluster in which four pairs of nickel atoms (the Ni...Ni distances in the pairs are nonequivalent and are equal to 2.826(2), 2.746(2), 2.724(2), and 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...Ni, 2 × 3.383(2) Å) through the tridentate oxygen atom (Ni—O, 2.045(8)—2.047(6) Å) and three bridging carboxylate groups (Ni—O, 1.997(6)—2.146(6) Å). Two terminal carboxylate groups are also bonded to this Ni atom (Ni—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,

Scheme 1



Reagents and conditions: *a*) an excess of dipy, MeCN, 20 °C; *b*) extraction with benzene, heptane, or hexane.

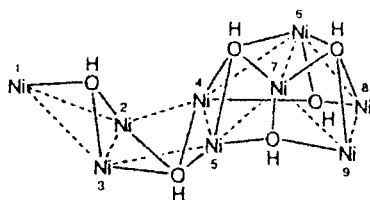


Fig. 1. Metal core of nine-nuclear complex 2.

which deviates from the Ni_4 plane (by 0.5151, 0.5111, and 0.6563 Å). The geometric characteristics of these fragments indicate that the O atoms belong to the hydroxy ligands, like the above-mentioned μ_3 -O atom that is located in the center of the terminal Ni_3 fragment (Ni(1), Ni(2), and Ni(3) atoms). Unfortunately, due to the large number of independent nonhydrogen atoms in this structure, H atoms could not be located from the X-ray data, 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 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.¹⁵ Magnetic measurements for cluster 2 (Fig. 1) in the 83–296 K range demonstrated that the effective magnetic moment per metal atom increases from 1.99 to 2.58 μ_B . The IR spectra of compound 2 have stretching vibration bands

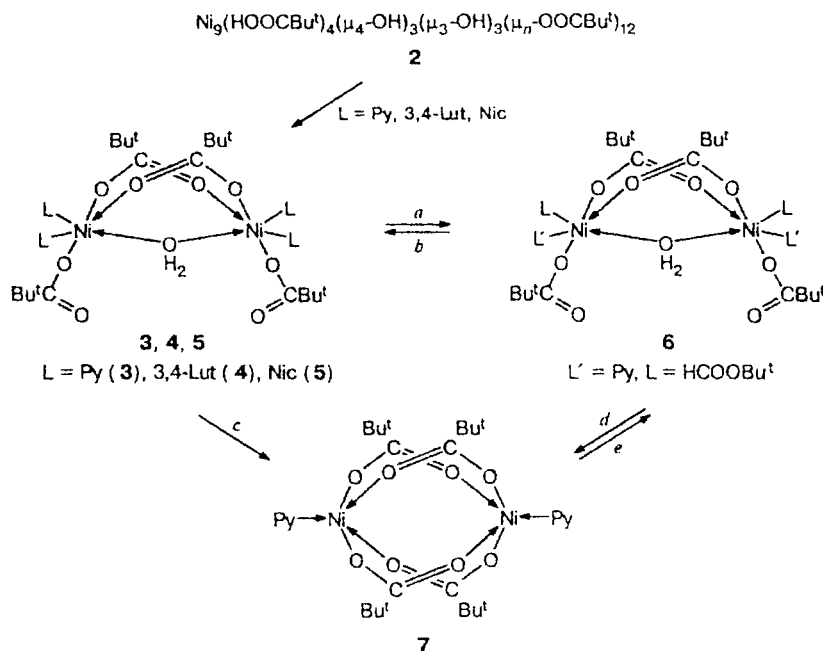
of the bridging carboxylate groups ($\nu_{sym} = 1573$ and 1610 cm^{-1} ; $\nu_{as} = 1369$ and 1425 cm^{-1}), the OCO fragments of the terminal-coordinated pivalic acid ($\nu_{OCO} = 1703\text{ cm}^{-1}$), and the OH groups (3457 cm^{-1}). The electronic absorption spectra of the complex in a THF solution and in the solid state are similar, which indicates that the structure of the complex remains unchanged in going from the crystal to the solution. Complex 2 appeared to be a convenient starting compound for preparing a series of nickel trimethylacetates with different numbers of nuclei in the metal core.

Trimethylacetate Ni^{II} complexes with pyridine bases

Binuclear nickel trimethylacetates with the fragments $Ni_2(\mu-OOCR)_2(\mu-OH_2)$ and $Ni_2(OOCR)_4$

Studies of the chemical reactivity of nine-nuclear complex 2 with respect to N-donor bases with different numbers of pyridine rings demonstrated that directed modifications of the structures of the final compounds can be rather smoothly performed according to the geometric characteristics and the chelating ability of the donor ligand and reaction conditions. Thus, complex 2 readily reacted with various bases containing one pyridine ring (Py, 3,4-lutidine (3,4-Lut), or *N*-nitroethoxynicotinamide (Nic)) to form blue crystals of adducts of the general formula $L_4Ni_2(OOCCMe_3)_2(\mu-OOCCMe_3)_2(\mu-OH_2)$ ($L =$

Scheme 2



Reagents and conditions: a) 110–140 °C, xylene; b) Py, 20–50 °C, benzene; c) solid KOH, benzene or MeCN; d) thermolysis of solid 6 *in vacuo*, 170 °C; e) 1 equiv. of H_2O , 2 equiv. of $HOCCMe_3$, benzene or heptane, 40–60 °C.

Py (3), 3,4-Lut (4), or Nic (5))¹⁵ (Scheme 2) in virtually quantitative yields.

According to the data of X-ray diffraction analysis, all the complexes in question have similar geometric characteristics of the binuclear metal fragments. Thus, the metal atoms in the molecules are located at nonbonding distances (Ni...Ni, 3.513(1) Å (3); 3.549(3) Å (4); 3.505(4) Å (5)). The ligand environments around the metal centers are nearly octahedral. Each nickel atom is bonded to the terminal (C—O, 1.237(4)—1.250(3) Å (3); 1.223(18)—1.261(16) Å (4); 1.231(19)—1.268(24) Å (5)) carboxylate group (Ni—O, 2.056(2) Å (3); 2.099(9) Å (4); 2.018(12)—2.062(13) Å (5)), to the two pyridine fragments (Ni—N, 2.104(3)—2.123(4) Å (3); 2.088(12)—2.103(9) Å (4); 2.125(15)—2.155(13) Å (5)), to two oxygen atoms of the bridging trimethylacetate groups (Ni—O, 2.012(2)—2.037(2) Å (3); 1.989(8)—2.023(9) Å (4); 1.999(12)—2.030(11) Å (5)), and to the oxygen atom of the bridging water molecule (Ni—O, 2.074(2)—2.078(3) Å (3); 2.104(6) Å (4); 2.077(12)—2.091(11) Å (5)); the Ni—O—Ni angle is 115.6(1)° (3), 114.9(2)° (4), and 114.4(5)° (5)). In the complexes under consideration, the Ni—O and Ni—N distances are close to the corresponding values observed in the previously reported carboxylates $L_2Ni_2(OOCR)_2(\mu-OOCR)_2(\mu-OH_2)$ ^{16,17} ($L = Py$, $R = 2-ClC_6H_4OCH_2$, Ni—N 2.104—2.113 Å; $L_2 = TMEDA$, $R = CF_3$, Ni—N 2.131—2.182 Å) and $L_2Ni_2(\mu-OOCR)_2(\mu-OH)^+$ ($L = N,N',N''$ -trimethyl-1,4,7-triazacyclononane, $R = Me$, Ni—N 2.136—2.169 Å)¹⁸ containing the same three-bridged Ni^{II} core. Previously,¹⁵ based on the data of thermomagnetic measurements of samples of 3—5, which were kept in air for several days, we suggested that these complexes contain Ni^{II} and Ni^{III} atoms. However, the refined magnetic data, which were obtained on a SQUID magnetometer in the temperature range of 2—300 K with the use of freshly prepared single-crystal samples, unambiguously indicated that these compounds contain only Ni^{II} atoms (for example, for a single crystal of complex 3 with dimensions of 2×2×1.5 mm the magnetic moment per Ni atom increased from 3.077 to 3.134 μ_B in the 300—20 K range and then decreased to 2.700 μ_B in the 20—2 K range). The difference in the magnetic properties of complex 3 that was stored in air and of a freshly prepared sample may be indicative of the possible structural changes that occur in the complexes upon storage. This leads not only to a loss of solubility, as we have noted previously,¹⁵ but also to a partial change in the electronic characteristics of the metal centers. However, the ferromagnetic type of spin-spin interactions between the metal ions and the spectral characteristics of the complexes remain unchanged.

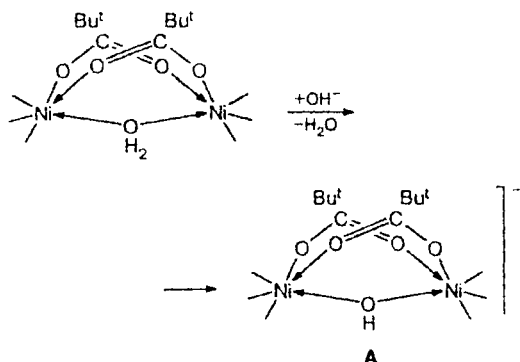
Solutions of complex 3 exhibit very unusual thermal properties. Thus, heating of 3 in xylene (110—140 °C) for 2—4 h resulted in elimination of two pyridine ligands to form the complex $Py_2Ni_2(HOCCMe_3)_2(OCCMe_3)_2(\mu-OCCMe_3)_2(\mu-OH_2)$ (6) (see Scheme 2). Molecule 6 contains two

metal atoms located at a nonbonding distance of 3.465(2) Å. In complex 6, the ligand environments around the nickel atoms are equivalent (nearly octahedral) as a result of coordination by the terminal molecules of pivalic acid (Ni—O, 2.142(5) Å), the carboxylate group (Ni—O, 2.069(5) Å), the pyridine ligand (Ni—N, 2.095(7) Å), the bridging oxygen atom of the water molecule (Ni—O, 2.106(4) Å), and the two oxygen atoms of the bridging trimethylacetate ligands (Ni—O, 1.992(5) and 1.983(5) Å). Note that the two last-mentioned distances are noticeably shorter than the values observed in the original compound 3. Complex 6, unlike ferromagnetic complex 3, is antiferromagnetic (μ_{eff}/Ni atom = 1.90—0.84 μ_B in the temperature range of 293—79 K, $-2J = 265$ cm⁻¹). When the reaction mixture containing complex 6 was cooled to 20 °C, the thermolysis products were virtually quantitatively converted into the original complex 3. Therefore, the reversible temperature-dependent ferromagnetic↔antiferromagnetic equilibrium actually occurs in solution.

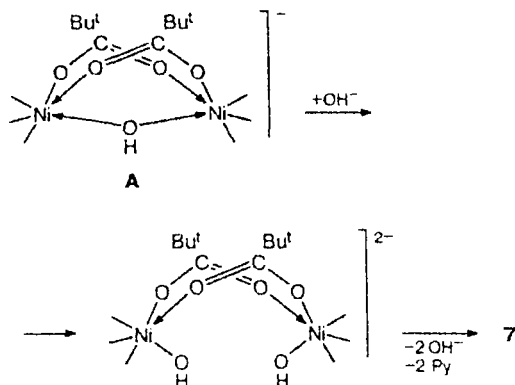
Complexes 3—6 contain an unusual bridging water molecule that formally has an "oxane" oxygen atom bonded to two nickel atoms and two hydrogen atoms (whose positions in complexes 3, 4, and 6 were located by X-ray diffraction analysis¹⁵) through covalent two-electron bonds. In complexes 3 and 4, the hydrogen atoms of the bridging H₂O molecule are involved in hydrogen bonding with the oxygen atoms of the terminal carboxylate groups, while in complex 6 this interaction is absent due to shielding of the hydrogen atoms of the aqua bridge by the coordinated pyridine molecules.¹⁵ In the structure with the maximum covalence of M—O and O—H bonds, the four-coordinated bridging oxygen atom in complexes 3—6 carries a positive charge +2. It is known that "hard" acid centers, such as aluminum and silicon, can form the above-mentioned "oxane" structures.^{19–22} To our knowledge, this coordination of the O atom is very rarely observed in the case of "soft" acid centers, such as Ni^{II}.^{16–18} This coordination of the O atom has not yet been observed in complexes of either palladium or platinum (two other members of the triad). Noteworthy is the strength of this bonding. The stable fragment Ni(μ -H₂O)Ni persists in both complexes 3 and 6 in spite of severe conditions of thermolysis and the presence of strongly basic pyridine molecules, which are capable of being strongly coordinated, in solutions (quantitative regeneration of complex 3 would otherwise be impossible). Apparently, the stability of the aqua dinickel fragment is the cause of the ligand exchange resulting in the replacement of one pyridine molecule by the terminal molecule of trimethylacetic acid to give complex 6. However, the yield of complex 6 was no more than 50%, which suggests the presence of other thermolysis products. However, attempts to isolate these products failed.

Complex 6 did not decompose in a decane solution up to 160 °C. Only when heated in the solid state *in vacuo* at 170 °C did complex 6 lose coordinated molecules of carboxylic acid and water to form the

binuclear antiferromagnetic Ni^{II} tetracarboxylate $\text{Py}_2\text{Ni}_2(\text{OCCMe}_3)_4$ (**7**). According to the data of X-ray diffraction analysis, this complex has the shortest Ni...Ni distance (2.603(2) Å) compared to the related nickel dimers with the lantern-like structure (in the known dimers $\text{L}_2\text{Ni}_2(\text{OCCMe}_3)_4$, where L = 2-methylquinoline,¹⁴ 2,4- $\text{Me}_2\text{C}_5\text{H}_3\text{N}$,¹³ 2,5- $\text{Me}_2\text{C}_5\text{H}_3\text{N}$,¹³ 2-Et $\text{C}_5\text{H}_4\text{N}$,¹⁴ or 2-picoline,¹² the Ni...Ni distances are 2.717–2.754 Å). The N–Ni...Ni–N fragment in complex **7** is linear (176.8(2)°). Complex **7** can be prepared by the reaction of compound **3** with solid KOH in benzene or MeCN at 80 °C (see Scheme 2) in high yield (70%). Under these conditions, two pyridine ligands and the bridging water molecule were displaced from the coordination sphere of the metal atoms. Note that it is the first example of the replacement under the action of a base, which seems to involve deprotonation of the bridging water molecule as the initial stage.



Subsequent interaction of hydroxide-bridged anionic complex **A** with the second equivalent of the nucleophile (OH^-) leads to the cleavage of the $\text{Ni}(\text{OH}^-)\text{Ni}$ bridge to form a complex containing only two carboxylate bridging ligands:

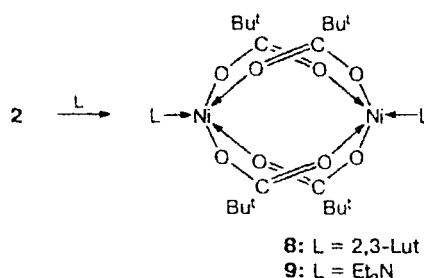


In the last stage, both OH groups of the ligand are replaced by the oxygen atoms of the terminal carboxy-

late groups to form structure **7** containing four bridging carboxylate groups. However, if the axial pyridine ligand does not contain α -substituents that stabilize the lantern-like structure,²³ complex **7** can again be converted into aqua-bridged complex **6** by the reaction with two equivalents of trimethylacetic acid and one equivalent of water in benzene or hexane at 80 °C (see Scheme 2).

Unlike the complex sequence of conversions $2 \rightarrow 3 \rightarrow 6 \rightarrow 7$, the binuclear four-bridged dinickel fragment with the lantern-like structure was readily formed (as was mentioned above) when α -substituted pyridine bases were used. Actually, the reaction of nine-nuclear complex **2** with 2,3-lutidine (2,3-Lut) immediately afforded the dimer (2,3- $\text{Me}_2\text{C}_5\text{H}_3\text{N}$) $_2\text{Ni}_2(\text{OCCMe}_3)_4$ (**8**) (Scheme 3). Like pyridine analog **7**, complex **8** is antiferromagnetic. However, the Ni...Ni distance (2.726(2) Å) in the non-linear N–Ni...Ni–N fragment (168.3(1)°) of **8** is substantially longer than that in **7** and is close to the corresponding values observed in the known trimethylacetate lantern-like dimers containing other α -substituted pyridines (Table 1).^{12–14}

Scheme 3



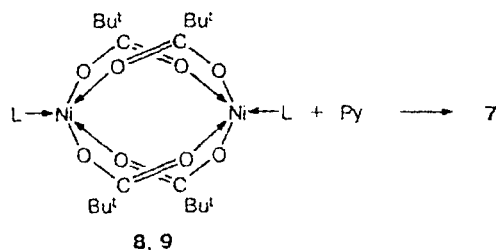
Reagents and conditions: L = 2,3-Lut or Et_3N ; benzene or hexane, 20 °C.

The binuclear complex with an analogous structure was unexpectedly obtained in the reaction of complex **2** with triethylamine (see Scheme 3). Apparently, this is due to a manifestation of steric factors of the bulky triethylamine base. In the last-mentioned case, these effects are probably more pronounced than in the above-mentioned α -substituted pyridines, due to which the antiferromagnetic four-bridged dimer (Et_3N) $_2\text{Ni}_2(\text{OCCMe}_3)_4$ (**9**) with the lantern-like structure was formed in one stage. In this complex, the Ni...Ni distance is rather large (2.728(2) Å), even though the N–Ni...Ni–N fragment is virtually linear (177.7(3)°). The Ni–N bond (2.106(6) Å) in complex **9** is noticeably weaker than those in the known dimeric trimethylacetates of this type containing α -substituted pyridines and all the more so with pyridine. This is confirmed not only by the bond length (Table 1) but also by the chemical properties of complex **9**. When boiled in benzene with 2,3-lutidine or pyridine, triethylamine

Table 1. The Ni...Ni and Ni—N distances (Å) in the lantern-like complexes $L_2Ni_2(OOCCMe_3)_4$

L	Ni...Ni	Ni—N	Reference
Py	2.603(2)	2.012(5)	25
2,3-Lut	2.726(2)	2.030(8)	25
2,4-Lut	2.721(1)	2.032(4)	13
2,5-Lut	2.7202(8)	2.034(3)	14
2-Methylquinoline	2.754(3)	2.047(9)	12
2-EtC ₅ H ₄ N	2.7227(7)	2.042(3)	14
2-Picoline	2.7171(7)	2.037(3)	14
Et ₃ N	2.728(2)	2.106(5)	21

dimer **9** readily lost coordinated Et₃N molecules to form complexes **8** and **7**, respectively, in quantitative yields. Analogously, the lutidine ligand in complex **8** can be replaced by the pyridine molecule (Scheme 4).

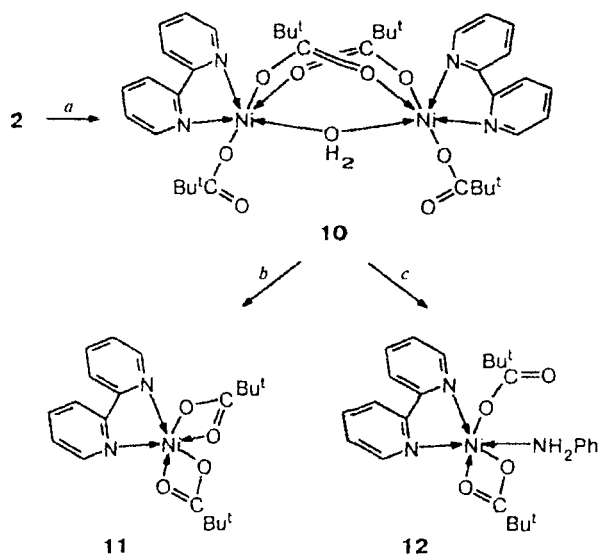
Scheme 4

Therefore, the reactivity of complex **9** offers considerable scope for the use of this compound in the synthesis of lantern-like trimethylacetate dimers with virtually all types of apical donor ligands, which are characterized by smaller values of the steric characteristics (for example, the Tolman angle²⁴) compared to those of triethylamine.

The reactions of 2,2'-dipyridyl that exhibit the strong chelating effect with transition-metal complexes generally afford monomers. However, the reaction of nine-nuclear complex **2** with dipyridyl gave the binuclear complex $dipy_2Ni_2(OOCCMe_3)_2(\mu-OOCCMe_3)_2(\mu-OH_2)$ (**10**) (Scheme 5) in high yield (60–70%).

The structure of the metal core in this compound is similar to those in compounds **3**–**5**. In complex **10**, the nickel atoms, which are located at large distances (Ni...Ni, 3.479(1) and 3.488(1) Å in two independent molecules), are linked by means of two bridging trimethylacetate groups (Ni—O, 2.009(3)–2.070(3) Å) and the bridging water molecule (Ni—O(H₂O), 2.092(3), 2.079(3) Å and 2.092(3), 2.089(3) Å; Ni—O—Ni, 113.0(1)° and 113.6(1)° in two independent molecules, respectively).²⁵ As in the case of complexes **3**–**5**, each metal atom in **10** is bonded to the terminal carboxylate group and two nitrogen atoms of the dipyridyl ligand.

In complex **10**, the pyridine rings of the dipyridyl ligand are located virtually in a single plane (the angle

Scheme 5

Reagents and conditions: a) dipy, benzene, 20 °C; b) thermolysis of solid complex **10** at 170 °C *in vacuo*; c) PhNH₂, hexane, 20 °C.

between these rings is 3.2(2)°, due to which the ligand environment around each Ni^{II} atom is somewhat distorted compared, for example, to pyridine derivative **3**, in which the angle between the pyridine ligands is 104.2(3)°. This difference in the environment has no essential effect on the magnetic properties of dipyridyl complex **10**. The latter also exhibits ferromagnetic properties ($g = 2.13$, $S_1 = S_2 = 1$, $J_1 = 2.0$ cm⁻¹) with a weak antiferromagnetic intermolecular interaction in the temperature range of 2–300 K ($ZJ^1 = -0.15$ cm⁻¹).

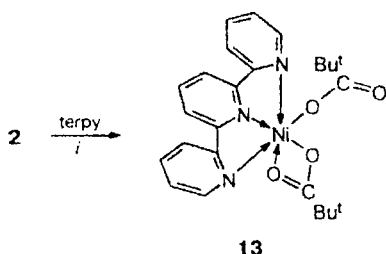
Mononuclear nickel trimethylacetates with 2,2'-dipyridyl and terpyridine

Unlike pyridine-coordinated complex **3**, dipyridyl-coordinated complex **10** is thermodynamically much more stable and does not decompose upon heating in xylene or decane up to 160 °C. Thermolysis of solid complex **10** resulted in elimination of the water molecule, but the chelate-bonded dipyridyl ligand that occupies two coordination sites was retained. In this case, the formation of the four-bridged lantern-like dimer is unfavorable, and thermolysis yielded the monomer $dipyNi(OOCCMe_3)_2$ (**11**) containing two chelate-coordinated trimethylacetate groups (Ni—N, 2.033(3), 2.059(4) Å and 2.0337(3), 2.052(5) Å; Ni—O, 2.106(4)–2.137(3) Å and 2.104(4)–2.135(4) Å in two independent molecules, respectively).²⁵ The monomer with four formally different ligands was formed in the reaction of complex **10** with aniline. In the resulting complex $dipyNi(NH_2Ph)(OOCCMe_3)_2$ (**12**) (Ni—N(dipy), 2.066(6), 2.075(5) Å and 2.053(6), 2.073(5) Å;

Ni—N(NH₂Ph), 2.097(4) and 2.113(4) Å in two independent molecules), which was isolated in almost quantitative yield, the trimethylacetate groups are coordinated differently, namely, as the terminal (Ni—O, 2.039(4) and 2.023(4) Å) and the chelate ligands (Ni—O, 2.194(4), 2.059(5) Å and 2.221(4), 2.070(5) Å)²⁵ (see Scheme 5).

The reaction of terpyridine (terpy) that has three pyridine rings with complex **2** immediately afforded the monomer (terpy)Ni(OCCMe₃)₂ (**13**)²⁵ (Scheme 6). Although the ligand environment around the nickel atom in **13** is analogous to that observed in monomer **12** (three nitrogen atoms and one oxygen atom are located in the equatorial plane and the OCCMe₃ groups are coordinated to the metal center as the terminal and chelate ligands), the Ni—N distances in the planar terpyridine ligand of complex **13** are noticeably non-equivalent. The bonds between the nickel atoms and the terminal nitrogen atoms (2.087(4) and 2.111(3) Å) are substantially elongated compared to the bond with the central N atom (1.991(4) Å).

Scheme 6



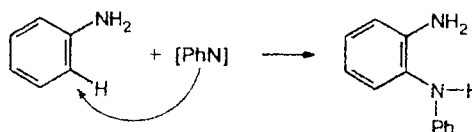
i. Benzene or heptane, 20 °C.

Probably, in consequence of the specific geometric characteristics of the terpyridine ligand (the nitrogen atoms are located virtually in the same line and all three rings are located in a single plane) in molecule **13** the electron density around the metal center is redistributed, which is reflected in the bonding of the nickel atom with the terminal carboxylate group, resulting in the strengthening of the Ni—O bond (1.994(3) Å). The parameters of the chelate metalocycle NiO₂CR (Ni—O, 2.073(4) and 2.176(2) Å) are analogous to those observed in compound **12**. All three monomers **11**–**13** are paramagnetic, which is typical of mononuclear Ni^{II} complexes. Their magnetic moments (3.12–3.09 μB; S = 1; g = 2.18) are temperature independent in the 77–300 K range.

Interactions of the nine-nuclear Ni^{II} cluster with organic mono- and diamines

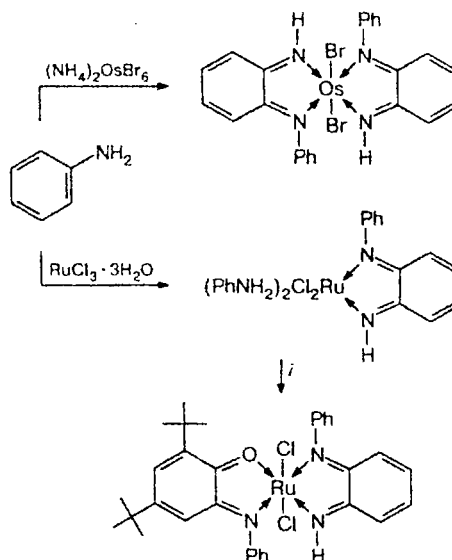
Unlike pyridine bases, primary amines contain two hydrogen atoms at the nitrogen atom. These bases can undergo deprotonation in the reactions with transition-

metal complexes and can be oxidized in the presence of an oxidizing agent to form new nitrogen-containing organic ligands. For example, in the reaction with the Os^{IV} ²⁶ or Ru^{III} ²⁷ complexes aniline was oxidized to form the *N*-phenyl-*o*-benzoquinonediimine ligand, 1,2-(NPh)(NH)C₆H₄, which is chelate-coordinated to the metal atom due to the presence of the lone electron pairs of two nitrogen atoms. It can be assumed that the aniline molecule in the coordination spheres of Ru^{III} and Os^{IV} enters into the reaction of oxidative dehydrogenation, in the course of which two H atoms are eliminated and the nitrene particle NPh is generated. Transition-metal complexes with the nitrene ligand NPh were obtained under certain conditions.²⁸ However, in this case the active particle is apparently inserted into the *ortho* C—H bond of the adjacent aniline molecule:



Further dehydrogenation of the resulting *N*-phenyl-*o*-phenylenediamine ligand (Scheme 7) afforded the products (PhNH₂)₂RuCl₂(1,2-(NH)(NPh)C₆H₄) and OsBr₂(1,2-(NH)(NPh)C₆H₄)₂ that were detected.

Scheme 7



i. 3,5-Di-*tert*-butylcatechol, MeOH, 20 °C.

In addition, the phenylnitrene that appears upon dehydrogenation of aniline can replace the oxygen atom in catechol, as is the case in the Ru^{II} complex,²⁹ to form a new N,O-donor ligand (see Scheme 7). These conver-

sions are very promising from the standpoint of assembly of complex organic molecules on metal centers. Consequently, we studied the chemical properties of nine-nuclear cluster **2** with respect to aniline and another primary amine, viz., propargylamine, containing the "soft" acetylene group along with the amino group.

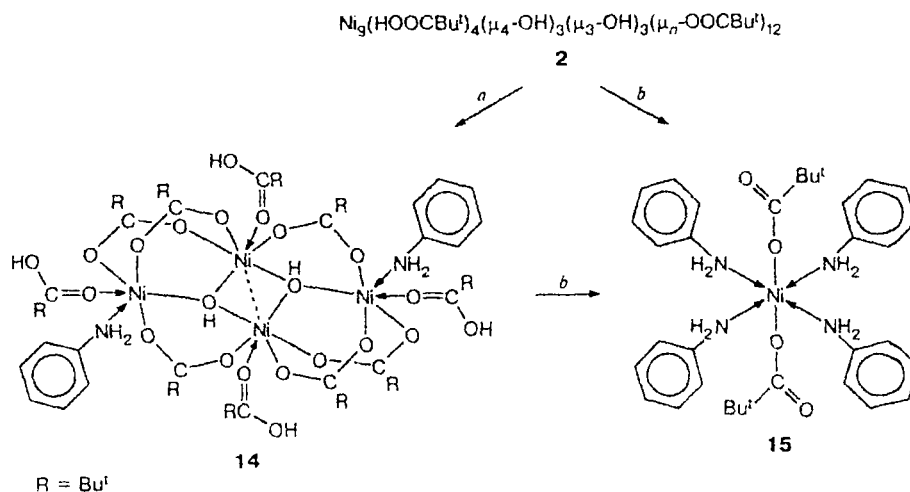
Trimethylacetate nickel complexes with aniline and propargylamine

The reaction of aniline with nine-nuclear complex **2** (the amine was taken in a deficient amount, aniline : Ni = 1 : 2) in benzene or MeCN gave the tetranuclear complex $(\text{PhNH}_2)_2\text{Ni}_4(\text{HOCCMe}_3)_4(\mu_3\text{-OH})_2(\mu\text{-OCCMe}_3)_6$ (**14**) containing Ni^{II} atoms (Scheme 8).³⁰ According to the data of X-ray diffraction analysis, the metal core of molecule **14** is a nearly planar distorted rhombus with nonequivalent Ni...Ni distances (the lengths of the opposite long and short sides of the rhombus are 3.525(1) and 3.333(1) Å, respectively). Each long side is supplemented with one trimethylacetate bridge (Ni—O, 2.011(3) and 2.011(3) Å; C—O, 1.248(6) and 1.250(6) Å), while the short sides have two carboxylate bridging ligands (Ni—O, 2.022(3)—2.108(3) Å). The tridentate-bridging hydroxy groups (Ni—O, 1.993(3) and 2.020(3) Å; O—H, 0.84(5) Å) are located above and below the triangular metal fragments of the Ni_4 rhombus. In addition, the two metal atoms located at the shorter axial distance (3.039(1) Å) contain the coordinated molecules of trimethylacetic acid (Ni—O, 2.166(3) Å; C—O, 1.224(5) and 1.307(6) Å), while the two other nickel atoms bear the coordinated aniline ligands (Ni—N, 2.132(4) Å; N—H, 0.93(5) and 0.83(5) Å) along with the coordinated molecules of pivalic acid (Ni—O, 2.153(3) Å; C—O, 1.204(6) and 1.308(6) Å). As a result, the coordination environment around each 20-electron metal atom is a distorted octahedron.

The reactions of an excess of aniline with cluster **2** or complex **14** resulted in decomposition of the polynuclear molecules and elimination of all hydroxy ligands and coordinated molecules of trimethylacetic acid to form the paramagnetic mononuclear complex $\text{L}_4\text{Ni}(\text{OCCMe}_3)_2$ (**15**, $\text{L} = \text{PhNH}_2$) (see Scheme 8) in virtually quantitative yield. According to the data of X-ray diffraction analysis of complex **15**, all four aniline ligands coordinated to the nickel atom are located in the equatorial plane (Ni—N, $2 \times 2.146(3)$ and $2 \times 2.171(3)$ Å; N—H, 0.618(8)—0.957(5) Å). The two monodentate trimethylacetate groups (Ni—O, $2 \times 2.035(2)$ Å; C—O, 1.278(5) and 1.254(4) Å; the O—C—O angle is $123.7(2)^\circ$) are located above and below this plane. As a result, the 20-electron nickel atom is in the typical octahedral environment. It should be also noted that complexes **14** and **15** were formed under an inert atmosphere as well as in air and are rather stable.³⁰ Apparently, the presence of a strong oxidizer is necessary for the generation of phenylnitrene from aniline followed by the formation of the *N*-phenyl-*o*-phenylenediimine ligand. Analogous reactions with osmium and ruthenium complexes were accompanied by reduction of the transition metal atoms in high oxidation states (Os^{IV} and Ru^{III}). In the case of nickel(II) trimethylacetates, the electronic state of the metal ions remains unchanged, and Ni^{II} possesses redox properties such that it cannot cause the above-mentioned conversions.

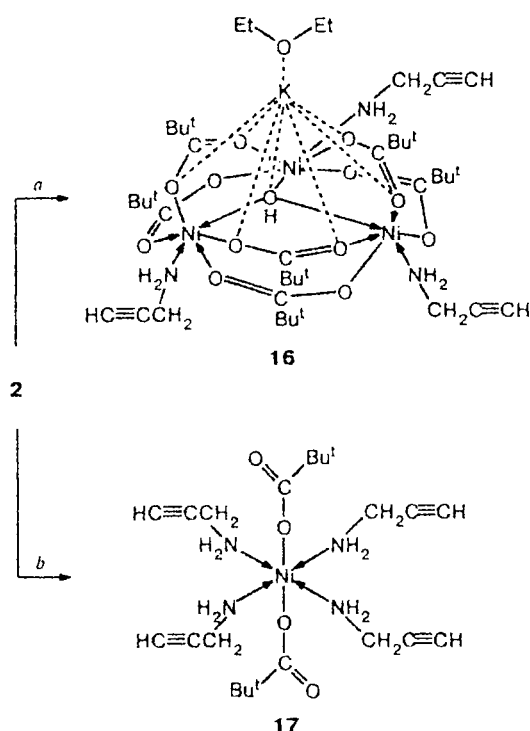
Unlike aniline, the reaction of complex **2** with propargylamine ($\text{L} : \text{Ni} = 1 : 2$ or $1 : 1$) in benzene or hexane did not afford tetramers. Only when this reaction was carried out with the use of solid KOH followed by extraction of the products with ether, was the very unstable complex $[(\text{HC}\equiv\text{CCH}_2\text{NH}_2)_3\text{Ni}_3(\mu_3\text{-OH})(\mu\text{-OCCMe}_3)_6][\text{K}(\text{OEt}_2)]$ (**16**) isolated as green prismatic crystals (yield 22%) (Scheme 9).

Scheme 8



Reagents and conditions: *a*) MeCN or benzene, 20–50 °C, $\text{L} : \text{Ni}_{\text{at}} = 1 : 2$; *b*) an excess of aniline.

Scheme 9



Reagents and conditions: a) 1) $\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$, 2) $\text{KOH}(\text{solid})$, Et_2O , 20°C ; b) an excess of $\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$.

X-ray diffraction analysis demonstrated that the core of the anion of complex **16** is the triangle formed by the nickel atoms ($\text{Ni}\dots\text{Ni}$, 3.492(1), 3.517(1), and 3.494(1) Å) with the oxygen atom of the hydroxy group located in the center ($\text{Ni}-\text{O}$, 2.021(4)–2.027(4) Å; the deviation of the oxygen atom from the Ni_3 plane is 0.12 Å). Each side of the Ni_3 triangle contains two bridging trimethylacetate groups. Each nickel atom is coordinated to the propargylamine molecule through the $\text{Ni}-\text{N}$ bond (2.065(8), 2.085(5), and 2.076(7) Å). Interestingly, the potassium atom, which is coordinated to the diethyl ether molecule ($\text{K}-\text{O}$, 2.742(7) Å), is located above the Ni_3O fragment ($\text{K}-\text{O}_{\text{center}}$, 2.864(4) Å) and interacts with six oxygen atoms of three carboxylate groups ($\text{K}-\text{O}$, 2.845(5)–2.922(5) Å).³¹

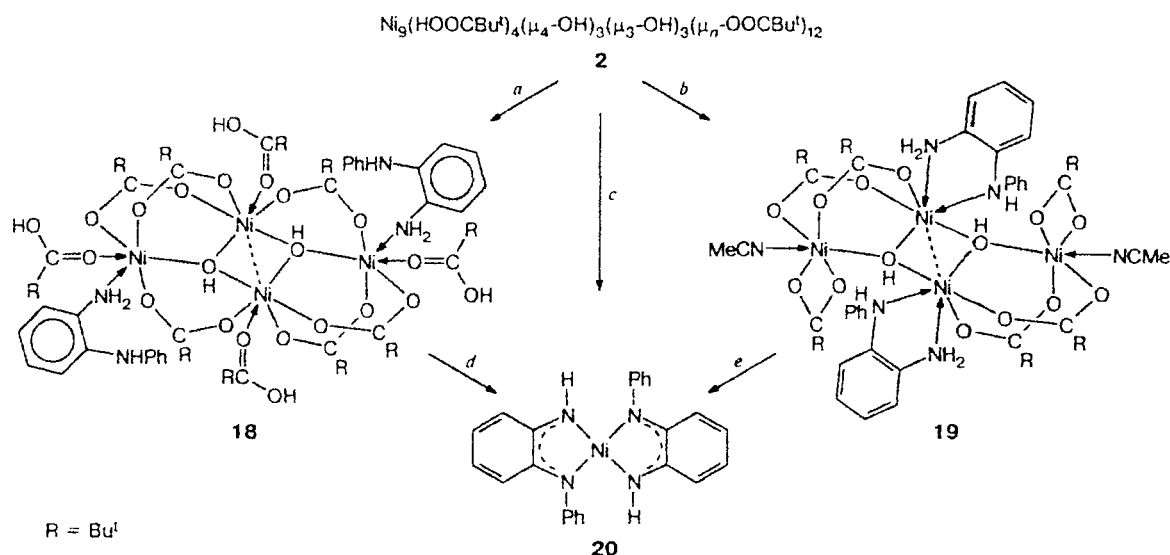
The reaction of an excess of propargylamine with nine-nuclear complex **2** afforded the monomeric complex $\text{L}_4\text{Ni}(\text{OOCMe}_3)_2$ (**17**, $\text{L} = \text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$), which is structurally similar to aniline-containing complex **15** (see Scheme 9). In complex **17**, the ligand environment around the metal atom is also an octahedron and all four propargyl ligands are coordinated to the Ni^{II} atom through the "hard" NH_2 group ($\text{Ni}-\text{N}$, $2\times 2.146(2)$ and $2\times 2.160(2)$ Å; $\text{N}-\text{H}$, 0.78(3)–0.96(4) Å; $\text{C}\equiv\text{C}$, $2\times 1.158(5)$ and $2\times 1.149(6)$ Å). The positions and geometric parameters of the carboxylate

groups in complex **17** ($\text{Ni}-\text{O}$, $2\times 2.059(1)$ Å; $\text{C}-\text{O}$, 1.270(3) and 1.241(2) Å; the $\text{O}-\text{C}-\text{O}$ angle is $123.7(2)^\circ$) differ only slightly from the corresponding values in molecule **15**. In the 78–300 K range, complexes **15** and **17** exhibit thermomagnetic properties typical of Ni^{II} monomers,^{10,11} and their effective magnetic moments (3.12 and 3.088 μB for **15** and **17**, respectively) are virtually temperature independent. At helium temperature (10–2 K), the magnetic moment of compound **15** sharply decreases to 2.746 μB , which is apparently due to the appearance of the antiferromagnetic intermolecular exchange. In the case of nickel carboxylate monomers, this effect was observed for the first time. Apparently, the scope of this effect and the role of the structural factors in the manifestation of this phenomenon calls for further investigation of this class of compounds.

Interaction of the nine-nuclear nickel complex with *N*-phenyl-*o*-phenylenediamine

In the case of a deficiency of the diamine ($\text{L} : \text{Ni} = 1 : 2$), the structures of the resulting complexes depend substantially on the conditions of the synthesis, in particular, on the solvent. For example, the reaction of complex **2** with 1,2- $(\text{NH}_2)(\text{HNPh})\text{C}_6\text{H}_4$ in nonpolar hexane or benzene afforded the tetranuclear complex (*o*- $\text{C}_6\text{H}_4\text{NH}_2\text{NHPh}$)₂ $\text{Ni}_4(\mu_3-\text{OH})_2(\text{HOOCMe}_3)_4(\mu\text{-OOCMe}_3)_6$ (**18**) isolated as green prismatic crystals³² (Scheme 10, reaction a). According to the data of X-ray diffraction analysis, the structure of complex **18** is virtually identical to that of aniline-containing tetramer **14**. The metal core of **18** is a planar Ni_4 distorted rhombic fragment (the $\text{Ni}\dots\text{Ni}$ distances are as follows: the opposite long sides of the rhombus are 3.533(2) and 3.532(2) Å; the opposite short sides are 3.309(2) Å and 3.315(2) Å; the axial $\text{Ni}\dots\text{Ni}$ distance is 3.045(2) Å). The $\mu_3-\text{OH}$ groups ($\text{Ni}-\text{O}$, 2.000(9)–2.033(9) Å) are located below and above the adjacent triangular planes of this rhombus. The short sides of the Ni_4 rhombus are additionally linked by pairs of the bridging carboxylate groups ($\text{Ni}-\text{O}$, 2.028(10)–2.116(10) Å), while each long side contains only one bridging OOCR group ($\text{Ni}-\text{O}$, 2.008(10)–2.032(10) Å). In addition, each metal atom is coordinated to the protonated molecules of pivalic acid, the $\text{Ni}-\text{O}$ distances (2.180(11)–2.208(11) Å) being substantially longer and the $\text{C}-\text{O}$ bond lengths in the corresponding OCO group being noticeably non-equivalent. In addition, in complex **18** the two nickel atoms that are located on the long diagonal of the metal rhombus are coordinated to the nitrogen atoms of the NH_2 groups of the two *N*-phenyl-*o*-phenylenediamine ligands ($\text{Ni}-\text{N}$, 2.158(12) and 2.137(12) Å). As a result, each Ni^{II} atom in cluster **18** is in a distorted octahedral ligand environment and formally has 20 electrons. The last-mentioned fact is apparently responsible for the substantial elongation of the bonds between the metal

Scheme 10

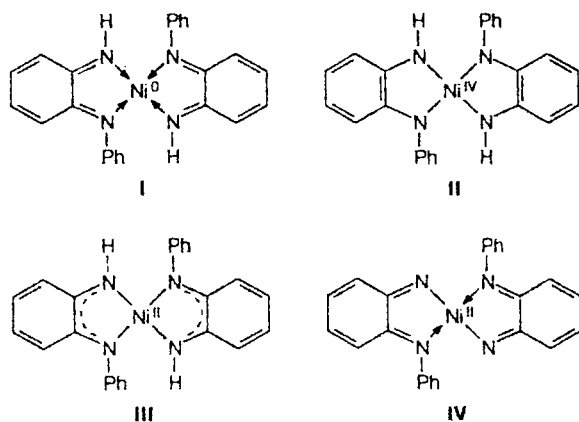


Reagents and conditions: a) benzene or heptane, 20–50 °C, $L : \text{Ni}_{\text{at}} = 1 : 2$; b) MeCN, 50–70 °C, $L : \text{Ni}_{\text{at}} = 1 : 2$; c, d, and e) an excess of diamine, KOH(solid).

atoms and the coordination centers of the terminal ligands, while, for example, in the four-bridged dimers $\text{L}_2\text{Ni}_2(\text{OCCMe}_3)_4$ (L is a pyridine base) containing 18-electron Ni^{II} atoms the Ni–N distances are noticeably shortened (see Table 1) (Ni–N, 2.034–2.041 Å). The magnetic behavior of complex **18** is similar to that of aniline-containing complex **14**, and its effective magnetic moment increases (from 3.15 to 3.30 μ_B) as the temperature decreases from 296 to 79 K, which is indicative of the ferromagnetic character of exchange interactions. The reaction of complex **2** with 1,2-(NH_2)(NHPh) C_6H_4 in MeCN³⁰ (see Scheme 10, reaction b) resulted in coordination of the second functional NHPH group to form the new tetranuclear complex $[\text{o-C}_6\text{H}_4(\text{NH}_2)(\text{NHPh})]_2\text{Ni}_4(\mu_3\text{-OH})_2(\text{MeCN})_2(\text{OCCMe}_3)_2(\mu\text{-OCCMe}_3)_4$ (**19**). In complex **19**, the diamine ligands are chelate-coordinated to the nickel atoms (Ni–N(NH_2), 2.134(2) Å; N–H, 0.975(25) and 0.897(45) Å; Ni–N(NHPh), 2.217(3) Å; N–H, 0.898(27) Å; N–C(Ph), 1.441(3) Å), which are located on the short axis of the metal rhombus (Ni...Ni, 3.101(1) Å), unlike tetramer **18** in which these ligands are monodentate-coordinated to the metal atoms that form the long diagonal. The metal core of the molecule remains planar. However, the opposite metal–metal distances corresponding to the sides of the rhombus differ even more substantially (the long and short Ni...Ni sides of the rhombus are $2 \times 3.774(1)$ and $2 \times 3.325(1)$ Å, respectively). As a result, the short sides of the metal core are supplemented with pairs of the carboxylate bridges (Ni–O, 1.993(2)–2.039(2) Å; C–O, 1.241(4)–1.262(5) Å), while the long sides have no external bridging ligands and are linked only through the tridentate

hydroxy groups, which are located inside the metal core above and below the triangular metal fragments (Ni–O, 2.020(2)–2.110(2) Å; O–H, 0.709(32) Å). In addition, the nickel atoms that form the long diagonal of the rhombus contain the coordinated acetonitrile ligands (Ni–N, 2.167(3) Å) and the chelate trimethylacetate ligands (Ni–O, 2.166(3) and 2.096(2) Å; C–O, 1.253(3) and 1.268(3) Å). In complex **19**, like compounds **14** and **18**, the 20-electron configurations and distorted octahedral ligand environments of the metal atoms are formally retained. In tetranuclear complex **19**, only the ligand field around the nickel atoms changes, which is noticeably reflected in the magnetic properties of this compound. Unlike ferromagnetic **14** and **18**, tetranuclear complex **19** is antiferromagnetic in the 4–300 K range. Its magnetic moment decreases monotonically as the temperature decreases, and only at 4–2 K does the magnetic moment slightly increase, which may be associated with the presence of a small admixture of the monomer or with the appearance of a weak ferromagnetic intermolecular exchange in this temperature range. Although detailed calculations of the exchange parameters can be performed only after the development of a special theoretical basis, the fact of a sharp change in the magnetic behavior of the complexes with the same $\text{M}_4(\mu\text{-OH})_2$ metal core, which frequently occurs in magnetic materials and applied catalysts, is quite obvious. This fact is of particular interest because hydroxy-bridged tetranuclear carboxylate complexes were obtained for Fe, Mn, and Co but were not found for Ni^{II} , which is a "catalytically active metal" and enters into the composition of various catalysts³³ and metal-containing enzymes (for example, urease^{3,6}).

N-Phenyl-*o*-phenylenediamine contains two amino groups (NH_2 and HNPh). The ability of these groups to undergo deprotonation is higher than that of amines of the aliphatic series (for example, of ethylenediamine) or of aniline. The reaction of cluster **2** with an excess of the *N*-phenyl-*o*-phenylenediamine ligand (**2** : **L** \cong 1 : 18) in a boiling solvent (benzene, heptane, hexane, or MeCN) in air afforded the mononuclear complex $\text{Ni}(\text{C}_6\text{H}_4(\text{NH})(\text{NPh}))_2$ (**20**) in an insignificant amount. However, when the reaction mixture was treated with a large excess of solid KOH, the yield of compound **20** was substantially higher even at -20°C (see Scheme 10). Under analogous conditions (an excess of **L** and KOH), the phenylenediamine ligand underwent deprotonation and complexes **18** and **19** were also converted into mononuclear complex **20** ($\text{Ni}-\text{N}$, 1.828(3)–1.863(4) Å). In complex **20**, both chelate deprotonated ligands have apparently the quinoid form. Thus, the C–C bonds in the phenylene rings are nonequivalent and four "long" and two "short" distances are clearly distinguished (1.415(6), 1.412(6), 1.406(6), and 1.423(6) (long distances) and 1.361(7) and 1.358(6) Å (short distances) and 1.426(6), 1.400(6), 1.408(7), and 1.407(6) (long distances) and 1.368(7) and 1.373(6) (short distances) Å in two independent molecules, respectively). The C–N bond lengths (1.364(5), 1.345(6) Å and 1.350(5), 1.345(6) Å in two independent molecules) in the planar fragment $\text{C}_6\text{H}_4\text{N}_2\text{NiN}_2\text{C}_6\text{H}_4$ are close to the lengths of the corresponding double bonds and are substantially smaller than the values observed for the single N–Ph bonds (1.436(5) and 1.443(5) Å in two independent molecules). The electronic structure of the ligand is still not evident. Since the presence of protons at nitrogen atoms cannot be unambiguously determined by X-ray diffraction analysis and NMR spectroscopy, several possible forms of this compound may be suggested by analogy with the known derivatives of *o*-phenylenediamine and maleonitrile.^{34,35}



One should take into account that complex **20** is diamagnetic and contains the 16-electron nickel(II) atom in the typical planar-square ligand environment. In this case, the formulas with the semiquinone (III) and com-

pletely deprotonated (IV) forms of the ligand seem to be the most probable. In the first case, the diamagnetism of the complex is a result of strong antiferromagnetic exchange between two paramagnetic centers formed due to the appearance of unpaired electrons on the ligands in the semiquinone form. Besides, the possibility of interconversion between these two structures (the semiquinone and the completely deprotonated) can not be excluded. Such interconversion is quite probable in a reaction medium containing proton donors, such as water, hydroxide ions, and trimethylacetic acid, which are formed in the course of the synthesis of complex **20**.

In conclusion, we emphasize that the data on the synthesis and chemical properties of nickel trimethylacetates demonstrate possibilities of the directed synthesis of these complexes. Compounds with different numbers of metal atoms in the cluster can be obtained by varying the geometric and electronic characteristics of N-donor organic molecules. This synthetic approach allows one to assemble complexes with a particular type of magnetic behavior (ferro- or antiferromagnetics) and to perform reversible transformations with a change in the type of spin-spin exchange interactions (ferromagnetic \rightleftharpoons antiferromagnetic). High yields of trimethylacetate complexes, their high solubility in various organic solvents, and high volatility give promise that complexes of this type may find use as starting compounds for preparing catalysts and various magnetic materials.

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