Letters to the Editor

Formation of a tetranuclear nickel(II) complex containing an unusual bridging ligand

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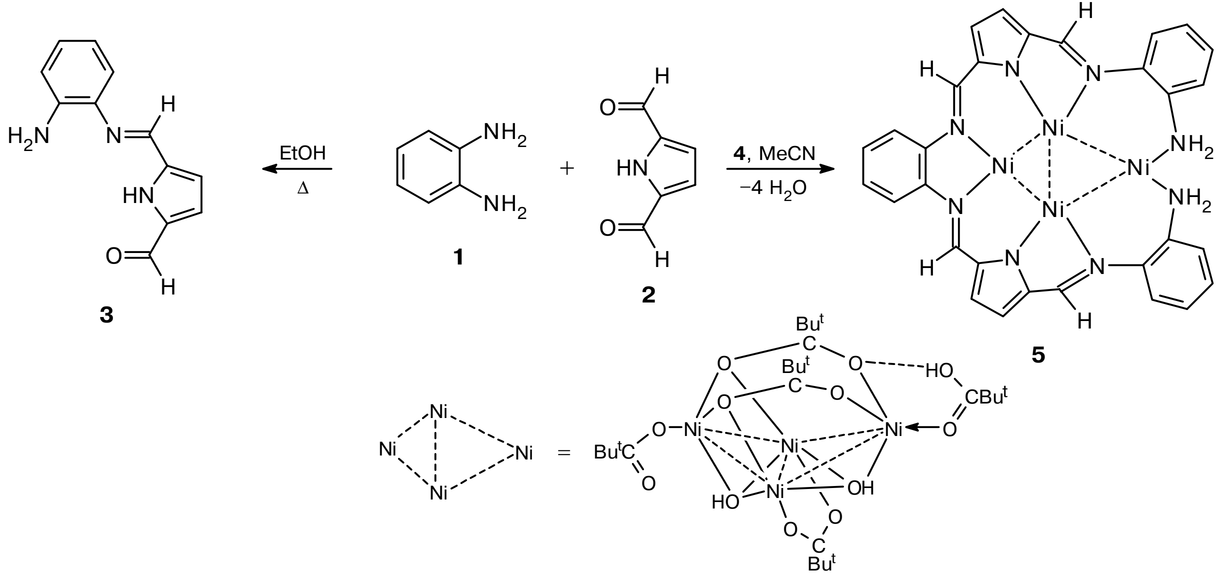
Recently, we have found that the reaction of *o*-phenylenediamine (**1**) with pyrrole-2,5-dicarbaldehyde[1] (**2**) in boiling EtOH afforded a yellow crystalline [1+1]-condensation product (**3**) in high yield.[2]

We have also found that an analogous reaction between compounds **1** and **2** in MeCN in the presence of the nonanuclear nickel complex $Ni_9(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCBu^t)_{12}$ (**4**)[3] (the reagent ratio was 9 : 9 : 1) gave rise to the tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)(\mu_3\text{-}OOCBu^t)_2(OOCBu^t)(HOOCBu^t) \cdot L$ (**5**) in high yield. The resulting complex contains a new unusual bridging ligand L, which is a product of condensation of three molecules **1** with two molecules **2**:



3 **1** **2** **5**

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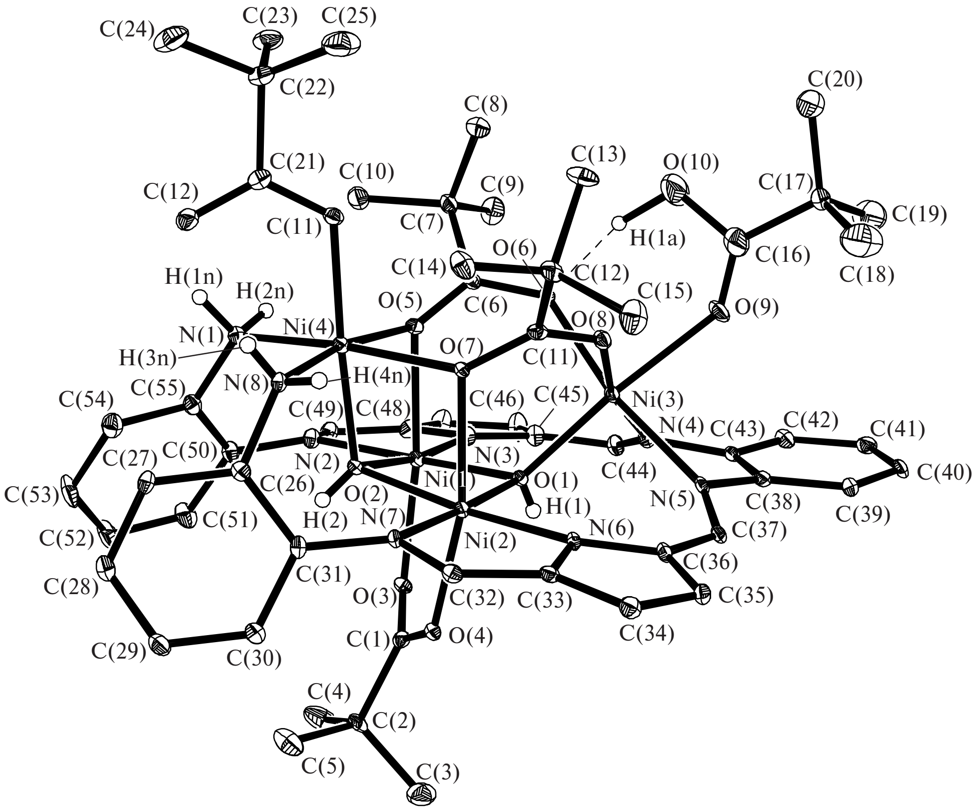

Fig. 1. Structure of complex **5**.

According to the results of X-ray diffraction study of dark-brown single crystals of solvate $\mathbf{5}\cdot MeCN$ (Fig. 1) (space group $P\bar{1}$, a = 12.948(2) Å, b = 13.604(3) Å, c = 18.706(4) Å, α = 98.458(4)°, β = 103.901(5)°, γ = 101.557(5)°, V = 3066.7(10) Å^3, Z = 2, ρ_{calc} = 1.422 g cm^{-3}, μ = 12.75 cm^{-1}, R_1 = 0.0574, wR_2 = 0.1430), four nickel atoms in the complex form a butterfly-like core with nonbonded metal—metal distances (Ni...Ni (axial), 2.9460(9) Å; Ni...Ni (of the wings), 3.129(1), 3.154(1), 3.436(1), and 3.440(1) Å). The metal atoms in complex **5** are linked through three bridging trimethylacetate groups and two μ_3-OH groups (Ni—O, 1.967(3)—2.017(3) Å). In addition, one of the peripheral metal atoms in the wingtip positions contains the terminal pivalate anion (Ni—O, 2.008(3) Å; C—O, 1.281(6) and 1.244(7) Å), whereas another metal atom bears the O atom of the monodentate-coordinated molecule of trimethylacetic acid (Ni—O, 2.155(3) Å; C—O, 1.135(8) and 1.410(10) Å) whose hydroxyl group is involved in hydrogen bonding (1.95(4) Å) with one of the O atom of the adjacent bridging trimethylacetate groups. Each metal atom is coordinated by the nitrogen atoms of the newly formed ligand L (Ni—N, 2.037(4)—2.092(4) Å; Ni—N(NH$_2$), 2.111(4)—2.140(4) Å), which encloses the cavity of the $Ni_4(\mu_3\text{-}OH)_2$ fragment. It should be noted that the new ligand retains two amino groups coordinated to one of the nickel atoms, which opens up additional possibilities for adding new units to the ligand (for example, by the condensation reaction) as well as for increasing the number of nuclei of the "internal" metal fragment. It should be noted that compound **5** possesses ferromagnetic properties (Fig. 2), which is untypical of nickel-containing carboxylate complexes.

All operations were carried out under an inert atmosphere using anhydrous MeCN. Pyrrole-2,5-dicarbaldehyde (**2**) was synthesized according to a known procedure.[1] The complex $Ni_9(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCBu^t)_{12}$ (**4**) was prepared according to a procedure reported previously.[3] The static

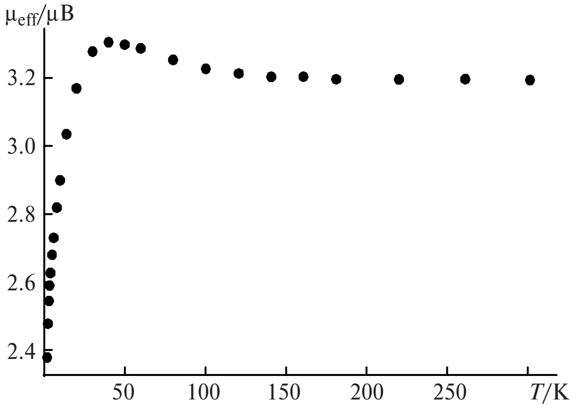

Fig. 2. Magnetic properties of complex **5** (μ_{eff} is the effective magnetic moment per Ni atom).

magnetic susceptibility was measured in the temperature range of 2—301 K on an MPMS-59 SQUID magnetometer at the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences. The IR spectrum was recorded on a Specord M 80 spectrophotometer in KBr pellets in the frequency range of 392—4000 cm^{-1}.

Synthesis of the complex $\mathbf{Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)(\mu_3\text{-}OOCBu^t)_2(OOCBu^t)(HOOCBu^t)\cdot L}$ (5). Dry compound **2** (127 mg, 1.035 mmol) and dry compound **1** (112 mg, 1.035 mmol) were successively added to a solution of complex **4** (260 mg, 0.115 mmol) in MeCN (70 mL). The reaction mixture was heated at 60 °C for 15 min. The resulting dark-red solution was concentrated to 15 mL at 60 °C (0.1 Torr) and kept at ~20 °C for 3 days. The dark-brown crystals that formed were separated from the solution by decantation, washed with cold MeCN, and dried *in vacuo* (22 °C, 0.1 Torr). The yield was 260 mg (43 %). Found (%): C, 51.97; H, 5.79; N, 9.51. $\mathrm{Ni_4O_{12}C_{57}N_9H_{75}}$. Calculated (%): C, 52.09; H, 5.71; N, 9.60. IR, ν/cm^{-1}: 3480 m, 3416 m, 2960 w, 2920 w, 2864 w, 1704 w, 1616 s, 1560 s, 1480 m, 1408 m, 1360 w, 1312 m, 1288 w, 1216 w, 1160 w, 1056 w, 960 w, 888 w, 752 m, 624 w, 608 w, 472 w.

The X-ray diffraction data were collected at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{\max} = 60°$) using a standard procedure.[4] A total of 10584 reflections were measured of which 9588 independent reflections had $F^2 > 2\sigma(I)$. The semiempirical absorption correction was applied.[5] The structure was solved by the direct method with the use of the SHELXS97 program package.[6] The positions and thermal parameters were refined anisotropically by the least-squares method using the SHELXL97 program package[7] (the positions of the H atoms were fixed with $U_\mathrm{H} = 0.08$ Å^2).

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