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Unusual condensation of 4,5-dimethyl-1,2-phenylenediamine with phthalaldehyde in the presence of Ni^{II} complexes giving rise to 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione*

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The reaction of 4,5-dimethyl-1,2-phenylenediamine (**1**) with phthalaldehyde (**2**) in the presence of Ni^{II} complexes afforded 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione (**3**), whose structure was established by X-ray diffraction analysis.

Key words: condensation, 4,5-dimethyl-1,2-phenylenediamine, phthalaldehyde, nickel(II) complexes.

The reactions of amines with aldehydes provide an efficient way of synthesizing Schiff's bases.[1,2] Compounds containing aryl groups at the nitrogen and carbon atoms are generally rather stable. These reactions can also be used for the preparation of heterocyclic compounds. An example is the Fridlender synthesis of quinoline.[3]

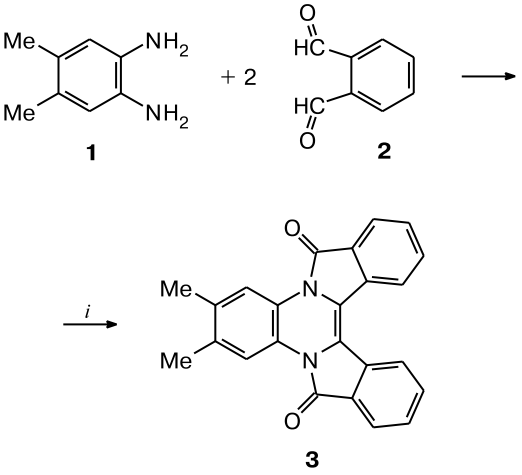
In attempting to synthesize a macrocyclic ligand from 4,5-dimethyl-1,2-phenylenediamine (**1**) and phthalaldehyde (**2**) in the presence of Ni^{II} compounds,[4] we unexpectedly found a new route of the reaction of dialdehydes with diamines giving rise to 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione (**3**) as one of the main products (Scheme 1).

The reaction of **1** with **2** in the presence of the nonanuclear hydroxopivalate cluster $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ [5] (**4**) (reagent ratio was 1 : 1 : 0.058) occurs in refluxing toluene under atmospheric oxygen.

Compound **3** can also be prepared with the use of $NiCl_2 \cdot 6H_2O$ in ethanol at 20 °C instead of cluster **4** in toluene. However, compound **3** was not generated in the absence of Ni^{II} complexes.

X-ray diffraction analysis showed that compound **3** is a fused system consisting of four six-membered rings and two five-membered rings (Fig. 1). Three peripheral six-membered rings are aromatic. The C—C bond lengths in these rings are typical of this class of molecules (1.370(5)—1.397(5) Å).[6] The central six-membered fragment contains two nitrogen atoms (N—C, 1.416(4)—1.427(4) Å), which are simultaneously involved in the adjacent fused five-membered rings containing the carbonyl groups (C=O, 1.225(4) Å).

Scheme 1



i. $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ (**4**), toluene, 110 °C.

From the formal viewpoint, compound **3** is a product of the reaction of one diamine molecule with two dialdehyde molecules. The results of our study demonstrated that the Ni^{II} atoms play the key role in the assembly of the molecule, organic reagents **1** and **2** being activated in the coordination spheres of the Ni^{II} atoms.

The reaction mechanism remains unclear. It should be noted that the analogous reactions with pyrrole-2,5-dialdehyde afforded macrocyclic Schiff's bases.[7,8]

Experimental

The nonanuclear $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ cluster was synthesized according to a

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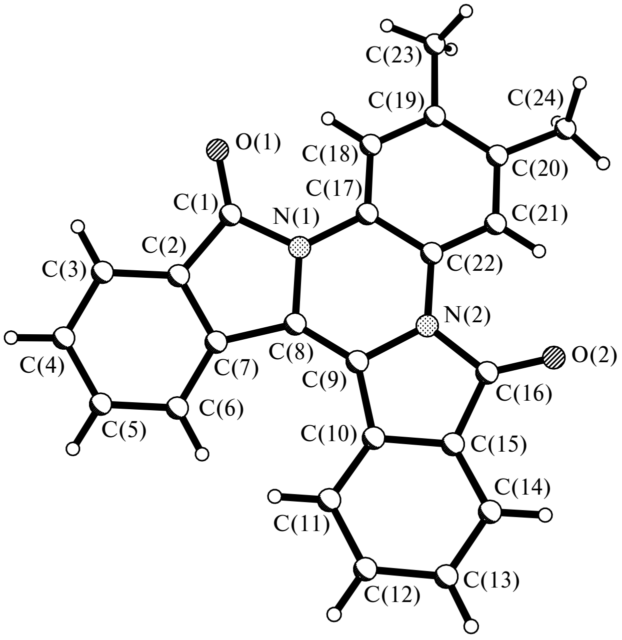

Fig. 1. Structure of compound **3**.

known procedure.[5] The IR spectra of the compounds were recorded on a Specord M80 instrument in KBr pellets.

4,5-Dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione (3). A mixture containing the $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ cluster (**4**) (0.6 g, 0.26 mmol), 4,5-dimethyl-1,2-phenylenediamine (**1**) (0.62 g, 4.5 mmol), and compound **2** (0.6 g, 4.6 mmol) in toluene (20 mL) was stirred in air at 110 °C for 0.5 h until the starting reagents were completely dissolved. The resulting red-brown solution was concentrated to 10 mL and transferred to a chromatographic column (Kiselgel 60, 5×20 cm). The red zone was eluted with ethanol (R_f = 0.9; 50 mL). The reaction solution was concentrated to 10 mL and kept at ~20 °C for 7 days. The red crystals that precipitated were separated from the solution by decantation, washed with cold ethanol, and dried in air. The yield of compound **3** was 0.17 g (20%). Found (%): C, 79.2; H, 4.47; N, 7.52. $C_{24}H_{16}N_2O_2$. Calculated (%): C, 79.12; H, 7.39; N, 7.69.

IR (KBr), ν/cm^{-1}: 3375 w, 2972 w, 2912 w, 1696 w, 1616 v.s, 1572 s, 1484 s, 1448 s, 1364 m, 1340 m, 1292 m, 1256 m, 1192 m, 1144 s, 1084 m, 1024 s, 996 m, 956 s, 904 s, 888 m, 836 m, 796 m, 748 w, 740 w, 688 v.s, 620 w, 588 w, 516 w, 492 w, 408 w. At room temperature, the reaction in ethanol with the use of $NiCl_2 \cdot 6H_2O$ gave compound **3** in 25% yield.

X-ray diffraction analysis of compound 3. The X-ray diffraction data were collected on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, −160 °C, ω scanning mode with a scan step of 0.3°, the frames were exposed for 30 s) using a standard procedure.[9] The structure was solved by direct methods with the use of the SHELX97 program package.[10] $C_{24}H_{16}N_2O_2$, M = 364.39, space group *Pbcn*, at T = −160 °C, a = 20.066(18) Å, b = 11.980(12) Å, c = 14.075(16) Å, V = 3383(6) $Å^3$, Z = 8, R_1 = 0.0529, wR_1 = 0.0778. The complete tables of the atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structural Database (No. 196699).

The X-ray diffraction study was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

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