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A macrocyclic ligand 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecine and its nickel(II) complex: Syntheses, reaction mechanism and structures

Xuan Shen [a,*], Lu Sun [a], Bo-Kun Jiang [a], Xin Wang [a], Akio Nakashima [b], Naoki Miyamoto [b], Kazunori Sakata [b], Yan Xu [a], Dun-Ru Zhu [a,*]

[a] State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China
[b] Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

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ABSTRACT

The template reaction of *o*-phenylenediamine, 1-benzoylacetone and nickelous acetate tetrahydrate results in two structure isomers, 6,17-dimethyl-8,15-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinatonickel (II) (**2**) and 6,15-dimethyl-8,17-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinatonickel (II) (**4**). However, the latter has been neglected in the previous research because of its low yield in the template reaction. The mechanism of this template reaction is discussed. Though the steric hindrance between the phenyl ring and the benzo ring in **2** is greater than that in **4**, the intermediate of the former shows better structural stability than that of the latter, leading to obviously higher final yield of **2** compared with that of **4**. *n*-Butyl alcohol is used artfully to separate the crude product of the template reaction into almost pure **2** and a mixture of **2** and **4** in a mole ratio of 1:5. The free base of **2**, 5,14-dihydro-6,17-dimethyl-8,15-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (**1**), can be synthesized by demetalization of **2** with gaseous HCl. The same treatment to the mixture of **2** and **4** in a mole ratio of 1:5 leads to the free base of **4**, 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (**3**). The neglected macrocyclic compounds **3** and **4** have been characterized unambiguously and their single-crystal structures have also been determined by X-ray diffraction analysis for the first time.

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Being similar to the catenulate Schiff base ligand 1,3-bis(salicylidene iminoethylamino)-2-propanol [1], 5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (H_2tmtaa), a versatile macrocyclic Schiff base ligand for transition and main group metal chemistry, has stimulated continuing interest in a wide range of chemical areas [2–4]. The extensive applications of H_2tmtaa and its complexes or their derivatives in fields of catalyst [5–11], sensor [12], conductive material [13,14], liquid crystal material [15], corrosive inhibitor [16] and DNA/RNA binding agents [17–19] show capacious research foreground of these macrocyclic compounds. 5,14-Dihydro-6,17-dimethyl-8,15-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (**1**, Fig. 1), which is an extension of H_2tmtaa's maternal analog by two phenyls, and the nickel (II) complex of **1**, 6,17-dimethyl-8,15-diphenyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecinatonickel (II) (**2**, Fig. 1), have been fully investigated [20–25]. However, syntheses and characterization of the isomeric macrocyclic compounds of **1** and **2**, 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (**3**, Fig. 1) and 6,15-dimethyl-8,17-diphenyldibenzo[*b*,*i*][1,4,8,11]tetraaza-cyclotetradecinatonickel (II) (**4**, Fig. 1), have not been reported unambiguously. The present study elucidates the syntheses and characterization of **3** and **4**. The reaction mechanism is discussed and the single-crystal structures of **3** and **4** are determined by X-ray diffraction analysis for the first time.

Recently, Chandra et al. reported the preparation of **3** by the direct condensation reaction of *o*-phenylenediamine and 1-benzoylacetone [26]. However, no cogent data can certify the production of the target compound. Furthermore, it has been made clear that this series of macrocyclic Schiff base ligands are synthesized by demetalization of their metal complexes prepared from the reaction of condensing *o*-phenylenediamines with β-diketones in the presence of metal ions (usually nickel (II)) [27]. The direct reaction of *o*-phenylenediamine and 1-benzoylacetone without the existence of metal ion leads to benzodiazepine instead of **1** or **3** (Scheme 1). In addition, Park et al. reported the template synthesis of **4** by the reaction of *o*-phenylenediamine, 1-benzoylacetone and nickelous acetate tetrahydrate ($NiAc_2 \cdot 4H_2O$). Nevertheless, judging from the synthetic method and ^{1}H NMR data, the product should be **2**, while not **4** [28, Fig. S2, S4].

1 and **2** were first reported by Eilmes et al. In their work, **1** was synthesized by the demetalization of **2** prepared from the template reaction of *o*-phenylenediamine, 1-benzoylacetone and $NiAc_2 \cdot 4H_2O$ [20]. The single-crystal structures of **1** and **2** were also determined by

* Corresponding authors. Tel.: +86 25 8358 7717; fax: +86 25 8336 5813.
E-mail addresses: shenxuan@njut.edu.cn (X. Shen), zhudr@njut.edu.cn (D.-R. Zhu).

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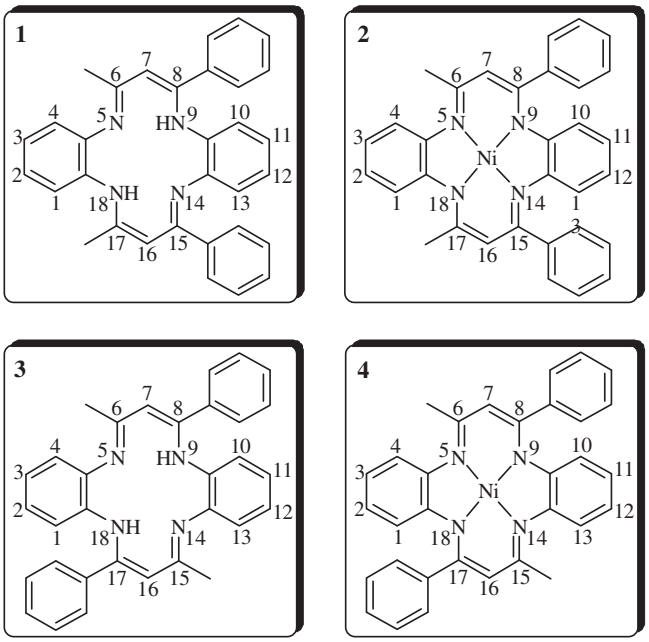
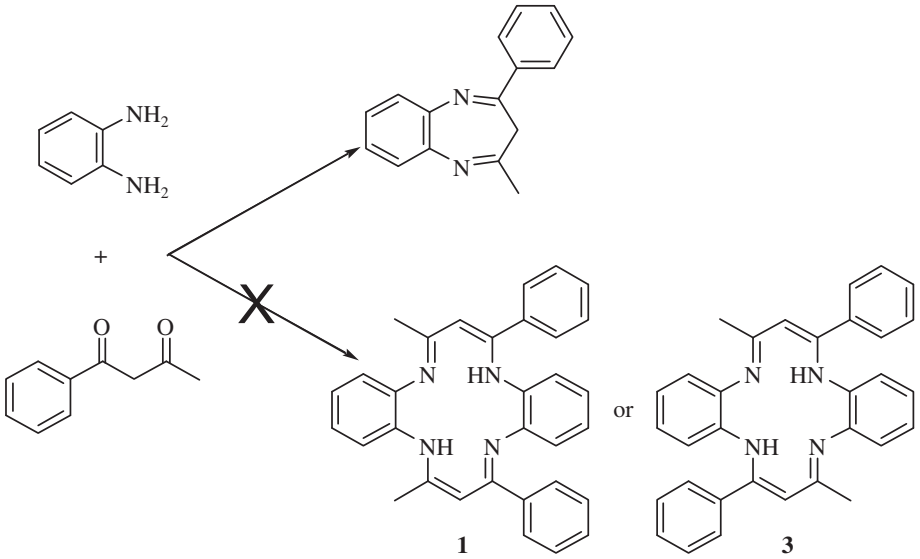


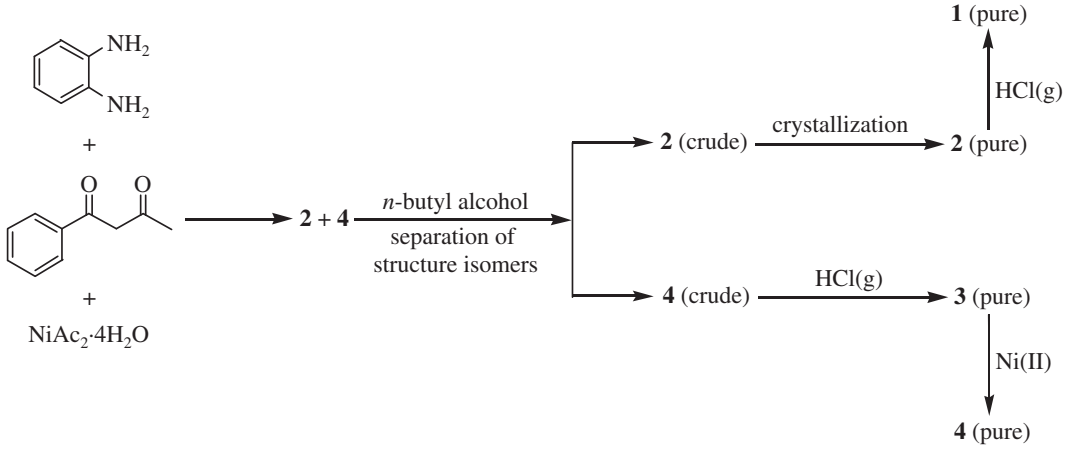
Fig. 1. Suggested structures of **1**–**4**.

the same researchers in their subsequent work [22]. However, syntheses and characterization of the structure isomers of **1**,**2**, **3** and **4**, were not mentioned in their work. In this template reaction, **2**'s structure isomer, **4**, should also yield theoretically at the same time. In this work, macrocyclic compounds **1**–**4** are synthesized according to the routes shown in Scheme 2. Treating the crude product of the template reaction with filtration, washing and chromatographic separation leads to a mixture of **2** and **4**. **2** and **4** cannot be separated absolutely by ordinary methods, even by chromatographic separation due to their extremely analogous physical and chemical properties. After unnumbered attempts, we detect that **2** and **4** show different solubility in some solvents, for instance, *n*-butyl alcohol. Thus, *n*-butyl alcohol is used to separate the mixture of **2** and **4** to give crude **2** in which the mole ratio of **2** and **4** is ca. 33:1 and crude **4** in which the mole ratio of **2** and **4** is ca. 1:5 [SI]. Pure **2** can be obtained by recrystallization of crude **2**, while pure **4** cannot be acquired in the same way because of the high content of **2** in crude **4**. Demetalization of pure **2** with gaseous HCl leads to pure **1** [SI]. Pure **3** can be obtained by demetalization of crude **4**[29] and pure **4** is able to be acquired by the reaction of **3** and $NiAc_2 \cdot 4H_2O$ in a high yield [30].

Generally speaking, the template reaction of *o*-phenylenediamine, 1-benzoylacetone and $NiAc_2 \cdot 4H_2O$ should result in **2** and **4** in a mole ration of 1:1 according to probability theory. However, the macrocyclic ligand **3** and its nickel(II) complex **4** have been neglected in the previous works. This may be due to the extremely low yield of **4** in the template reaction. The possible mechanism of the formation of **2** and **4** in the template reaction of *o*-phenylenediamine, 1-benzoylacetone and $NiAc_2 \cdot 4H_2O$ is shown in Scheme 3. The first reaction step is that two 1-



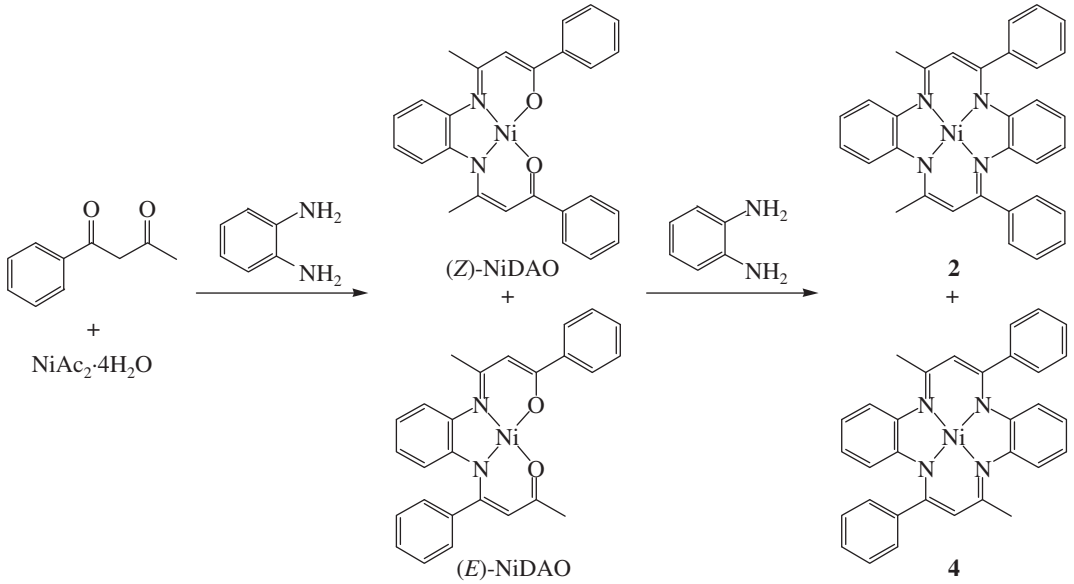
Scheme 1. The condensation reaction of *o*-phenylenediamine and 1-benzoylacetone.



Scheme 2. Synthetic routes of **1**–**4**.

benzoylacetone molecules react with one *o*-phenylenediamine molecule and one $NiAc_2 \cdot 4H_2O$ molecule, leading to the intermediates, (*Z*)-NiDAO and (*E*)-NiDAO. Existence and characterization of (*Z*)-NiDAO have been reported [22]. Secondly, the reaction of (*Z*)-NiDAO or (*E*)-NiDAO with another *o*-phenylenediamine molecule results in corresponding macrocyclic compound **2** or **4**. Because two phenyl substituents in **2** are in the *cis* positions and those in **4** are in the *trans* positions, the steric hindrance between phenyl ring and benzo ring in **2** should be greater than that in **4**. Thus, it seems that **4** can be presumed as the more stable product of the template reaction and the yield of **4** in the reaction should be higher. However, judging from the structures of the intermediates, (*Z*)-NiDAO and (*E*)-NiDAO, the former should be the more stable product, because in order to overcome the steric hindrance, two phenyl rings have a trend depart from the benzo ring. Thus, (*Z*)-NiDAO is the chief product and (*E*)-NiDAO is the secondary product in the first step of the template reaction, which leading the higher final yield of **2** than **4**. Methanol, ethanol, *n*-butyl alcohol and 2-methoxyl ethanol are used as reaction solvents respectively and the template reactions are carried out under reflux. It can be found that with the rise of the reaction temperature, the mole ratio of **4** in the product will also rise. Nevertheless, high reaction temperature will lead to the decomposition of the intermediates and cause the total yield of **2** and **4** to decrease [Table S2]. Thus, considering these factors synthetically, ethanol has been selected as the reaction solvent for the template reaction and **4** is obtained in a relatively high yield.

3 crystallizes in the triclinic space group *P*-1 [31] with two similar molecules in the asymmetric unit (Figs. 2 and 3). Two phenyl substituents in **3** are adjacent to two different benzo rings, while those in **1** are adjacent to the same benzo ring. Being similar to this series of macrocyclic compounds, both molecules **A** and **B** show a saddle-shaped deformation of the macrocycle because of the mutual repulsion of the methyl, phenyl and benzo groups, while exhibiting a distincter guache conformation compared with that of **1**. Being very different from the unsubstituted highly π-conjugated macrocyclic H_2tmtaa or its derivatives, four N atoms in **3** show great uncoplanarity. Δ_{max} values of N atoms in molecules **A** and **B** are 0.676 and 0.568 Å, respectively. This may be due to the great distorting effect of the methyl and phenyl substituents to the N_4 plane. Meanwhile, the great distorting effect also enlarges the dihedral angles of the almost flat N_4 plane and other



Scheme 3. The possible mechanism of the formation of **2** and **4** in the template reaction of *o*-phenylenediamine, 1-benzoylacetone and $NiAc_2 \cdot 4H_2O$.

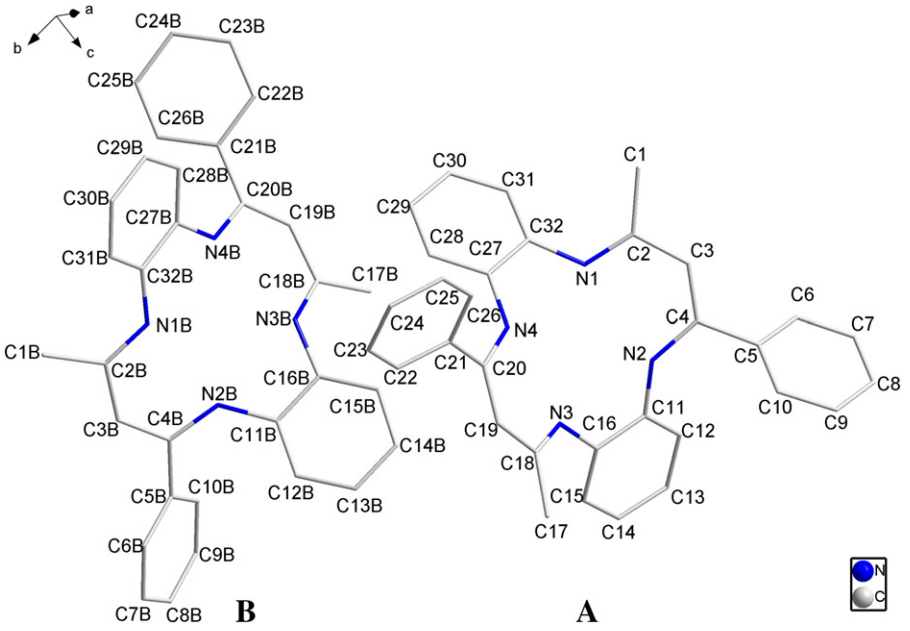


Fig. 2. Partial view of the unit cell of **3**, showing two similar molecules (**A** (right) and **B** (left)) in the asymmetric unit. Selected bond distances (Å) and angles (°) for **A** and **B**: N1 – C2 1.305(10) (**A**) 1.310(9) (**B**), N2 – C4 1.364(10) (**A**) 1.360(9) (**B**), N3 – C18 1.295(10) (**A**) 1.312(10) (**B**), N4 – C20 1.355(9) (**A**) 1.367(9) (**B**), C4 – C5 1.506(11) (**A**) 1.477(11) (**B**), C20 – C21 1.483(11) (**A**), 1.471(11) (**B**); C2 – N1 – C32 124.2(6) (**A**) 124.4(6) (**B**), C4 – N2 – C11 131.1(6) (**A**) 129.5(6) (**B**), C18 – N3 – C16 125.6(6) (**A**) 124.5(6) (**B**), C20 – N4 – C27 133.1(7) (**A**) 130.0(6) (**B**), N1 – C2 – C3 119.9(7) (**A**) 118.7(7) (**B**), C2 – C3 – C4 127.3(7) (**A**) 128.6(7) (**B**), C3 – C4 – N2 121.5(7) (**A**) 120.1(7) (**B**), N3 – C18 – C19 121.2(7) (**A**) 119.5(7) (**B**), C18 – C19 – C20 127.0(7) (**A**) 128.1(7) (**B**), C19 – C20 – N4 121.4(7) (**A**) 119.7(7) (**B**).

planes of the macrocycle: ∠([N_4] – [N1 – C32 – C27 – N4]) = 29.00° (**A**) (25.53° (**B**)), ∠([N_4] – [N2 – C11 – C16 – N3]) = 26.77° (**A**) (26.99° (**B**)), ∠([N_4] – [C(11 – 16)]) = 33.23° (**A**) (33.28° (**B**)), ∠([N_4] – [C (27 – 32)]) = 35.99° (**A**) (31.63° (**B**)), ∠([N_4] – [N1 – C2 – C4 – N2]) = 22.89° (**A**) (21.41° (**B**)), ∠([N_4] – [N3 – C18 – C20 – N4]) = 25.37° (**A**) (24.76° (**B**)), ∠([N_4] – [C2 – C3 – C4]) = 25.59° (A) (20.52° (**B**)), ∠([N_4] – [C18 – C19 – C20]) = 25.37° (**A**) (27.66° (**B**)), ∠([N_4] – [C(5–10)]) = 40.31° (**A**) (39.94° (**B**)), ∠([N_4] – [C(21–26)]) = 44.79° (**A**) (34.91° (**B**)). Though the aforementioned dihedral angles in **1** and **3** show considerable difference, for example, the dihedral angles of the benzo rings and the N_4 plane in **3** are larger than those in **1**, while the dihedral angles of the diiminato fragments and the N_4 plane in **3** are smaller than those in **1**, both **1** and **3** keep the optimal conformations to overcome the steric hindrance between the multiple substituents and the macrocycles. In **3**, two NH groups are on the side of the phenyl substituents. Thus, C2 – N1, C18 – N3 are imino C═N bonds and C4 – N2, C20 – N4 are amino C – N bonds. These results can also be verified by the lengths of the corresponding bonds. The bond lengths of C2 – N1 and C18 – N3 are 1.305 and 1.295 Å (**A**) (1.310 and 1.312 Å (**B**)), respectively, which are obviously shorter than those of C4 – N2 and C20 – N4 (1.364 and 1.355 Å (**A**), 1.360 and 1.367 Å (**B**)). Furthermore, imino N1 and N3 including C – N – C bond angle values (C2 – N1 – C32 124.2° (**A**) 124.4° (**B**), C18 – N3 – C16 125.6° (**A**) 124.5° (**B**)) are obviously smaller than amino N2 and N4 including ones (C4 – N2 – C11 131.1° (**A**) 129.5° (**B**),

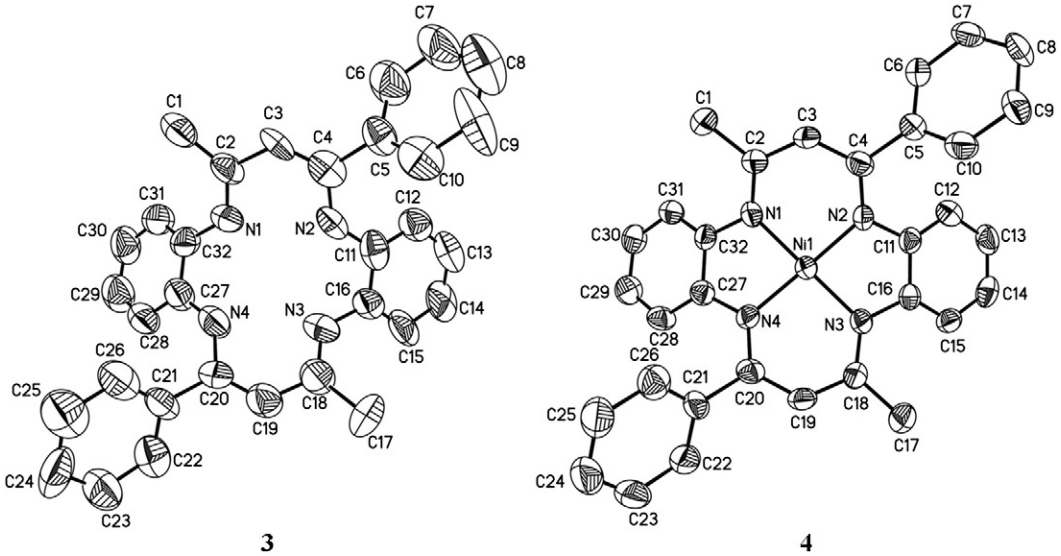


Fig. 3. ORTEP drawings of **3** (left) and **4** (right). The H atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **4**: Ni1 – N1 1.870(3), Ni1 – N2 1.848(3), Ni1 – N3 1.880(3), Ni1 – N4 1.853(3), N1 – C2 1.330(4), N2 – C4 1.348(4), N3 – C18 1.326(4), N4 – C20 1.347(4), C4 – C5 1.491(5), C20 – C21 1.496(5); N1 – Ni1 – N3 176.29(12), N2 – Ni1 – N4 175.24(12), N1 – Ni1 – N2 94.45(12), N2 – Ni1 – N3 85.48(12), N3 – Ni1 – N4 95.86(12), N4 – Ni1 – N1 84.52(12).

C20 – N4 – C27 133.1° (**A**) 130.0° (**B**)). The N_4 'core size' of **3** is 2.040 Å (**A**) (2.002 Å (**B**)), which is smaller than that of **1** (2.260 Å) [22] and is bigger than that of H_2tmtaa (1.902 Å) [3].

4 is obtained from the reaction of $NiAc_2 \cdot 4H_2O$ and **3** in which two N atoms are replaced by one Ni atom. **4** crystallizes in the monoclinic space group $P2_1/n$ [31]. ORTEP view of **4** is shown in Fig. 3. **4** assumes the same saddle-shaped conformation of **3** with two benzo rings and two diiminato fragments pointing to opposite directions. However, almost all dihedral angles of the N_4 plane and other planes of the macrocycle are smaller than corresponding ones of **3**, implying the flattening effect of Ni atom to the saddle-shaped molecule. Though Ni atom lies at the near center of the N_4 plane and has a trend of flattening the molecule, the coplanarity of four N atoms in the almost flat N_4 plane is still not very good with the N atoms Δ_{max} value of 0.273 Å. This may be due to the strong distorting effect of the methyl and phenyl substituents to the N_4 plane. The average Ni – N bond distance is 1.863 Å, while the lengths of Ni – N bonds including imino N (Ni1 – N1 1.870 and Ni1 – N3 1.880 Å) are longer than those including amino N (Ni1 – N2 1.848 and Ni1 – N4 1.853 Å), corresponding to bigger N1 – Ni1 – N3 angle (176.29°) with respect to N2 – Ni1 – N4 angle (175.24°). The N – Ni – N angles in the five-member ring (N4 – Ni1 – N1 84.52 and N2 – Ni1 – N3 85.48°) are smaller than those in the six-member (N1 – Ni1 – N2 94.45 and N3 – Ni1 – N4 95.86°), being similar to those of **2** [22]. Compared with **3**, the lengths of C – N bonds in two diiminato fragments are all shortened, however, those on the side of the methyl substituents (N1 – C2 1.330 and N3 – C18 1.326 Å) are howbeit shorter than those on the side of the phenyl substituents (N2 – C4 1.348 and N4 – C20 1.347 Å).

In summary, because of the unstability of the corresponding intermediate in the template reaction of *o*-phenylenediamine, 1-benzoylacetone and $NiAc_2 \cdot 4H_2O$, the yield of **4** is extremely lower than that of its structure isomer, **2**, leading to the negligence of **4** in previous works. *n*-Butyl alcohol has been artfully used to purify **4** from the crude product of the template reaction. **3**, the macrocyclic free base of **4**, has also been synthesized and characterized unambiguously. The single-crystal structures **3** and **4** have also been determined by X-ray diffraction analysis for the first time. Because of the flattening effect of Ni atom in **4**, the distortion of **4** is not as hard as that of **3**. The discovery of **3** and **4** will expend the research field of this series of macrocyclic compounds.

Acknowledgments

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Appendix A. Supplementary material

CCDC 657136 and 764814 contain the supplementary crystallographic data for compounds **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.05.040.

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[29] Synthesis of **3**: a mixture of **2** and **4** in a mole ratio of 1:5 (3.009 g, 5.73 mmol) and ethanol (100 mL) were added in a 200 mL three-necked flask to form a suspension. With the cooling of water bath, hydrogen chloride gas was blown slowly into the stirred suspension as far as the color of the solution changed and

yellow-white precipitates appeared. After the reaction mixture was stirred overnight at room temperature, the solid was collected by filtration and washed with ethanol. Then this hydrochloride was dissolved in distilled water. After the insoluble residues were removed by filtration, the filtrate was neutralized by adding potassium carbonate to give dark orange precipitates. Then the neutralized suspension was poured into a separating funnel and extracted with 50 mL dichloromethane three times. After being dried with magnesium sulfate, the extract was evaporated to give powder. Dissolving the powder in dichloromethane formed a saturated solution in which a little hexane was then added. The mixture was allowed to stand overnight at room temperature to give tawny block crystals of **3** which were suitable for X-ray crystal structure analysis in a yield of 1.281 g (47.7%). Anal. Calc. for **3** ($C_{32}H_{28}N_4$, 468.23): C, 82.02; H, 6.02; N, 11.96. Found: C, 81.93.15; H, 6.07; N, 11.95%. M.p.: 268–271 °C (DSC). IR (KBr, cm^{-1}): ν(C═C, C═N) 1612, 1551, 1508, 1450. FAB^+ MS: 469 $(M+1)^+$. ^1H NMR (400 MHz, $CDCl_3$) (ppm): δ 12.68 (s, 2H, NH), 7.36–7.40 (m, 10H, C_6H_5), 6.90 (m, 2H, C_6H_4), 6.83 (m, 2H, C_6H_4), 6.63 (m, 2H, C_6H_4), 6.23 (m, 2H, C_6H_4), 5.16 (s, 2H, CH), 2.32 (s, 6H, CH_3).

[30] Synthesis of **4**: after ethanol (70 mL) and $NiAc_2\cdot 4H_2O$ (0.801 g, 3.21 mmol) were added in a 200 mL three-necked flask, the mixture was heated with stirring as far as the solids dissolved completely. Then a solution of **3** (1.254 g, 2.67 mmol) in chloroform was slowly added dropwise and the reaction mixture was refluxed for 2 h. The solvent was removed by evaporation and the product was purified and separated on an alumina chromatographic column using chloroform as elutriant. After the filtrate was reduced to ca. 20 mL by evaporation, 20 mL acetone was further added in. The solution was allowed to stand overnight at room temperature to give dark green crystals of **3** in a yield of 1.351 g (96.3%). Perfect crystals were chosen out for X-ray crystal structure analysis. Anal. Calc. for **4** ($C_{32}H_{26}N_4Ni$, 524.15): C, 73.17; H, 4.99; N, 10.67. Found: C, 73.24; H, 4.91; N, 10.55%. M.p.: 385–388 °C (DSC). IR (KBr, cm^{-1}): ν(C═C, C═N) 1539, 1514, 1472, 1366. FAB^+ MS: 525 $(M+1)^+$. ^1H NMR (400 MHz, $CDCl_3$) (ppm): δ 7.33 (m, 10H, C_6H_5), 6.75 (m, 2H, C_6H_4), 6.41 (m, 2H, C_6H_4), 6.16 (m, 2H, C_6H_4), 5.67 (m, 2H, C_6H_4), 5.03 (s, 2H, CH), 2.22 (s, 6H, CH_3).

[31] Crystallographic data for **3**: $C_{32}H_{28}N_4$, $M_r=468.60$, triclinic *P*-1 with $a=11.207(3)$ Å, $b=11.602(9)$ Å, $c=19.546(6)$ Å, $\alpha=89.95(4)^o$, $\beta=92.27(2)^o$, $\gamma=98.64(4)^o$, $V=2511(2)$ Å^3, $Z=4$, $D_c=1.240$ g cm^{-3}, $F(000)=992$, $GOF=0.975$, $R_1=0.0575$, $\omega R_2=0.2033$, ($I>2\sigma(I)$), $R_1=0.0617$, $\omega R_2=0.2186$ (all data). Crystallographic data for **4**: $C_{32}H_{26}N_4Ni$, $M_r=525.28$, monoclinic $P2_1/n$ with $a=8.9847(14)$ Å, $b=10.5286(16)$ Å, $c=26.155(4)$ Å, $\beta=98.726(2)^o$, $V=2445.5(7)$ Å^3, $Z=4$, $D_c=1.427$ g cm^{-3}, $F(000)=1096$, $GOF=1.014$, $R_1=0.0453$, $\omega R_2=0.1038$, ($I>2\sigma(I)$), $R_1=0.0815$, $\omega R_2=0.1258$ (all data).