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# Theoretical modeling of the molecular and crystal structures and a square-planar to tetrahedral conformational rearrangement of *trans*-planar bis(*N*-methylsalicylaldiminato)nickel(II)

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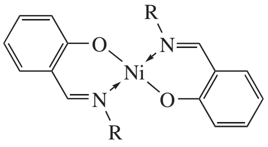
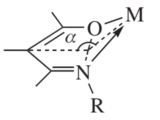
**The DFT B3LYP/6-311++g(d,p)/6-31g(d,p) calculations performed on bis(*N*-methylsalicylaldiminato)nickel(II), its isomers and clusters containing up to ten molecules of the complex have shown that the metal chelate rings are intrinsically planar and their step-like distortion observed in the solid state is caused by the factors relevant to the crystal packing conditions.**

Stereochemical non-rigidity and low energy barrier conformational rearrangements of isomerizations of bis(*N*-R-salicylaldiminato)nickel(II) **1** and other transition metal complexes have attracted much attention.[1] Nonetheless, problems concerned with the origin of the factors that define the molecular structure of the complexes of this type remain unsolved or to be the subject of controversy. Such is the long debated question on the relative role of electronic, steric and crystal packing factors responsible for the folding of the metal chelate rings of complexes **1** and their analogues (**1**, M = Cu, Pd) along the N…O line (the ladder rung distortion **1a**).



**1**

R = Alk, Ar

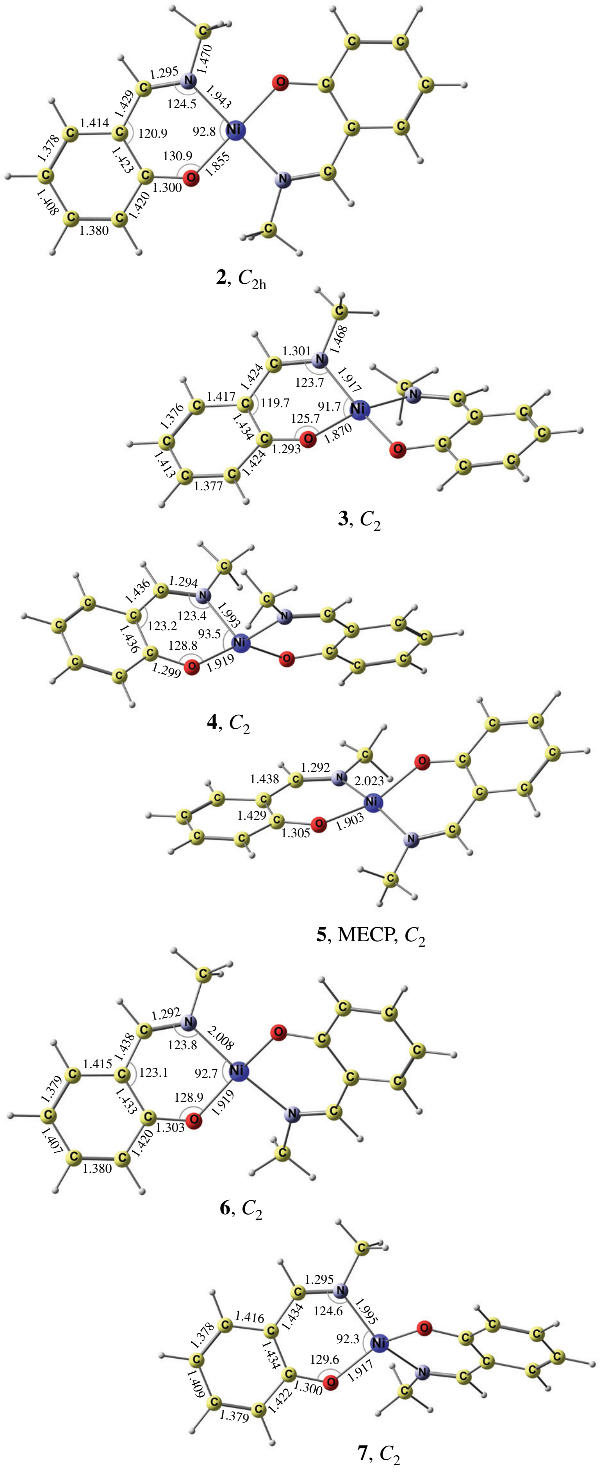


**1a**

The analysis of the problem is complicated by the lack in coordination of the experimental studies of the molecular structure of complexes **1**. Thus, for bis(*N*-methylsalicylaldiminato)nickel(II) **1** (R = Me) the Cambridge Structural Database contains more than ten results of the X-ray determinations concluded in either planar[2] or the step-like distorted[3] structure of its metal chelate rings. The goal of this work was to apply the currently most appropriate theoretical techniques to the study of the molecular structure of **1** (R = Me) as an isolated molecule and in the associate of ten molecules reproducing the structures of crystal cells found for two different modes of crystal packing. We have also calculated relative stability of the *cis*-planar and *pseudo*-tetrahedral isomers of **1** (R = Me) and studied the reaction path for the square-planar to tetrahedral isomerization of the metal chelate complex. The calculations have been performed using the Gaussian 03 system of programs[4] at the DFT B3LYP/6-311++g(d,p)/6-31g(d,p) level.[5] For the study of the spin-forbidden square-planar to tetrahedral isomerization of **1** (R = Me), the methods[6] developed for the study of reaction paths of processes associated with the alteration of spin state based on the determination of a minimum energy crossing point (MECP) on the seam of intersecting lowest singlet and triplet potential energy surfaces (PESs) and recently applied to the study of the rearrangement between the diamagnetic and paramagnetic forms of the close structural analogues of **1** (R = Me)[7] have been employed.

As was shown by the B3LYP/6-311++g(d,p) calculations carried out with full geometry optimization and the frequency verification, the global minimum on the ground state singlet PES of **1** (R = Me) is represented by the *trans*-planar structure of **2**, which is 13.4 kcal mol$^{-1}$ energy favourable compared with the *cis*-planar isomer **3** (Figure 1). No stationary point on the PES that would correspond to the stepped structure was found by the calculations. This finding suggests that such a distortion is not caused by electronic factors or steric demands inherent in the isolated molecule of **1** (R = Me). The *pseudo*-tetrahedral structure of **4** corresponds to the global minimum on the lowest triplet PES of the complex. It is only 2.9 kcal mol$^{-1}$ less energy favourable than **2**, which fact well agrees with the dynamic equilibrium of these forms observed in solution. The energy barrier to the rearrangement between the two conformers was evaluated as the height of the MECP, where the change in the spin state of a molecule (crossover) occurs at the intersection of the minimal energy reaction paths located on singlet and triplet PESs (Figure 2). The computed low value (6.2 kcal mol$^{-1}$) is in accord with the experimental data on this extremely fast spin-forbidden reaction.[1(*a*)] The steepest descent from the MECP of **5** along the triplet and singlet PESs leads to two minima corresponding to square-planar (**2**) and *pseudo*-tetrahedral (**6**) structures. The structure of **6** corresponding to a local minimum on the triplet PES is an intermediate preceding the formation of **4** *via* transition state **7**. The energy profile depicting these transformations is shown in Figure 2.

To examine the problem of how the packing of molecules **1** (R = Me) affects details of their molecular structure, the DFT [B3LYP/6-31g(d,p)] calculations of the clusters containing up to ten molecules of the complex have been carried out. The starting geometries were chosen from the X-ray determinations[8] obtained for two polymorphic modifications of **1** (R = Me) with *trans*-planar (CSD Refcode MSLDNI16) and distorted (CSD Refcode MSLDNI17) structures. The full geometry optimization (opt=loose mode) gave rise to the structures of **8** and **9**, respectively (Figure 3). The molecules placed within the central parts of the clusters maintain the same structures as in the corre-



**2**, $C_{2h}$

**3**, $C_2$

**4**, $C_2$

**5**, MECP, $C_2$

**6**, $C_2$

**7**, $C_2$

**Figure 1** Optimized geometries of *trans*-planar **2**, *cis*-planar **3** and two *pseudo*-tetrahedral **4** and **6** isomers of **1** (R = Me), transition state **7** for the **4** $\rightleftharpoons$ **6** isomerization and the structure of MECP **5** on the reaction path for the spin-forbidden square-planar to tetrahedral conformational isomerization **2** $\rightleftharpoons$ **6** $\rightleftharpoons$ **4**. Here and after bond lengths and angles are given in Å and degrees, respectively.

sponding crystal cells of the complex, whereas those disposed along the edges have substantially distorted structures. The molecular geometries calculated for the centrally located molecules of **8′** and **9′** virtually coincide with those experimentally determined. Associate **9** with the step-like distorted molecules is 3.6 kcal mol$^{-1}$ (0.4 kcal mol$^{-1}$ as scaled to a molecule) energy preferred to **8**.

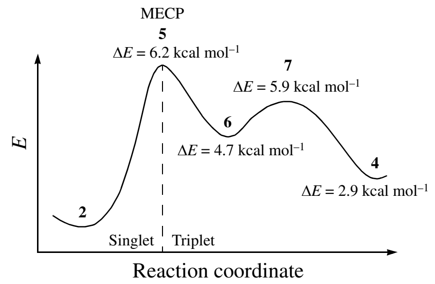
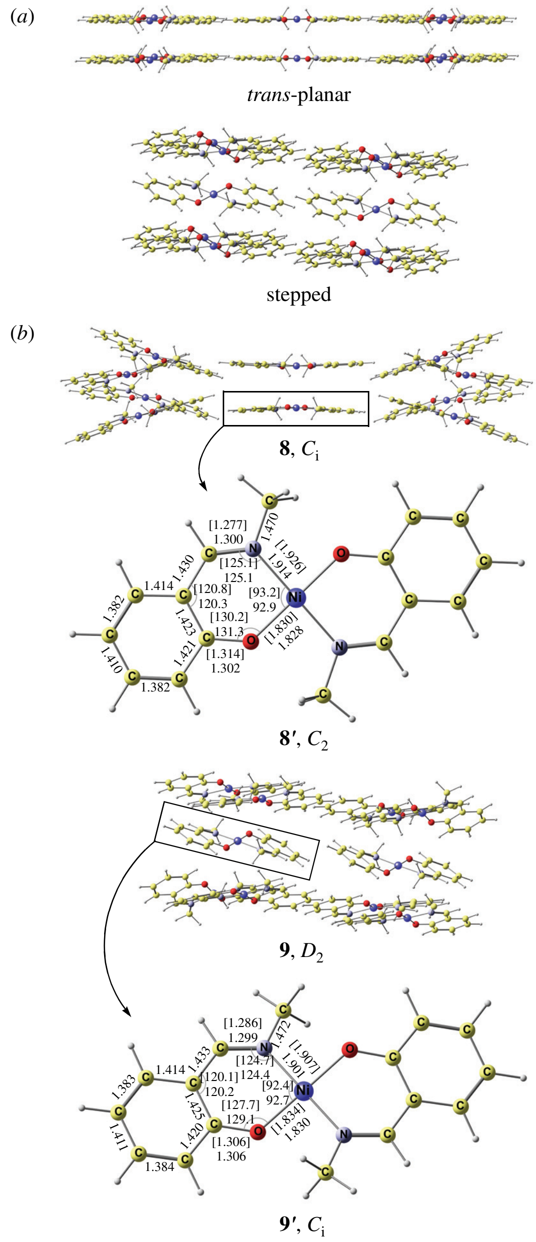


**Figure 2** Energy profile for the spin-forbidden square-planar to tetrahedral conformational isomerization **2** $\rightleftharpoons$ **4** of **1** (R = Me).



(*a*)

*trans*-planar

stepped

(*b*)

**8**, $C_i$

**8′**, $C_2$

**9**, $D_2$

**9′**, $C_i$

**Figure 3** (*a*) The crystal cell structures for two polymorphs of bis(*N*-methylsalicylaldiminato)nickel(II) **1** (R = Me) with *trans*-planar and stepped molecular configurations. (*b*) The DFT [B3LYP/6-31g(d,p)] computed geometries of the clusters of **8** and **9** composed of ten molecules of **1** (R = Me) with the initial planar and distorted molecular configurations. **8′** and **9′** – calculated and X-ray determined[8] (shown in brackets) geometries of the centrally disposed molecules. The angle α calculated for **9′** is equivalent to 162°.

Therefore we can conclude that the metal chelate rings of bis(*N*-methylsalicylaldiminato)nickel(II) **1** (R = Me) are intrinsically planar and their step-like distortion observed in the solid state is caused by the factors relevant to the crystal packing conditions, which may be reliably reproduced only by calculations of molecular associates comprising sufficiently large number of metal chelate molecules.

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