Two nickel complexes, namely, mer-[Ni(dien)2](NO3)2 (I) and mer-[Ni(dien)2]Cl2.H2O (II), have been synthesized under ambient conditions, where (dien = diethylenetriamine = bis(2-aminoethyl) amine and mer = meridional coordination). Their crystal and molecular structures have been determined by single-crystal X-ray diffraction methods. The complex (I) crystallizes in the orthorhombic system, space group Pbca (no, 61), Z = 8, with a = 8.8117(6) Å, b = 14.0023(8) Å, c = 26.7603(17) Å, V = 3301.79 Å³ for (I), The complex (II) crystallizes in the monoclinic system, space group P21/c (no 14) a = 13.5000(4) Å, b = 8.7170(3) Å, c = 13.9430(4) Å, V = 1604.41 Å³ for (II). Meridional (mer) coordination promotes the generation of larger and lower-symmetry prismatic structures, in contrast with the facial (fac) coordination and higher-symmetry. For the complexes (I) and (II), the structures are formed by the cation [Ni(C4H13N3)2]2+, two nitrate anions for (I) and two chloride anions and water molecule for (II). The nickel (II) atom is coordinated to six nitrogen donors from two neutral dien ligands, adopting a slightly distorted octahedral geometry. The newly complexes were also characterized by Infrared, TGA-DTA analysis and UV–Vis spectroscopy. Vibrational analysis of the two complexes was realized by infrared spectroscopy, which confirmed the characteristic bands of diethylenetriamine and nitrate groups. The morphology and the size of the two nickel complexes were monitored by scanning electron microscopy (SEM). Moreover, the thermal behaviour of the complexes was investigated, and the calcination of the two complexes under air has led to the production of Ni/NiO nanoparticles.