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Introduction

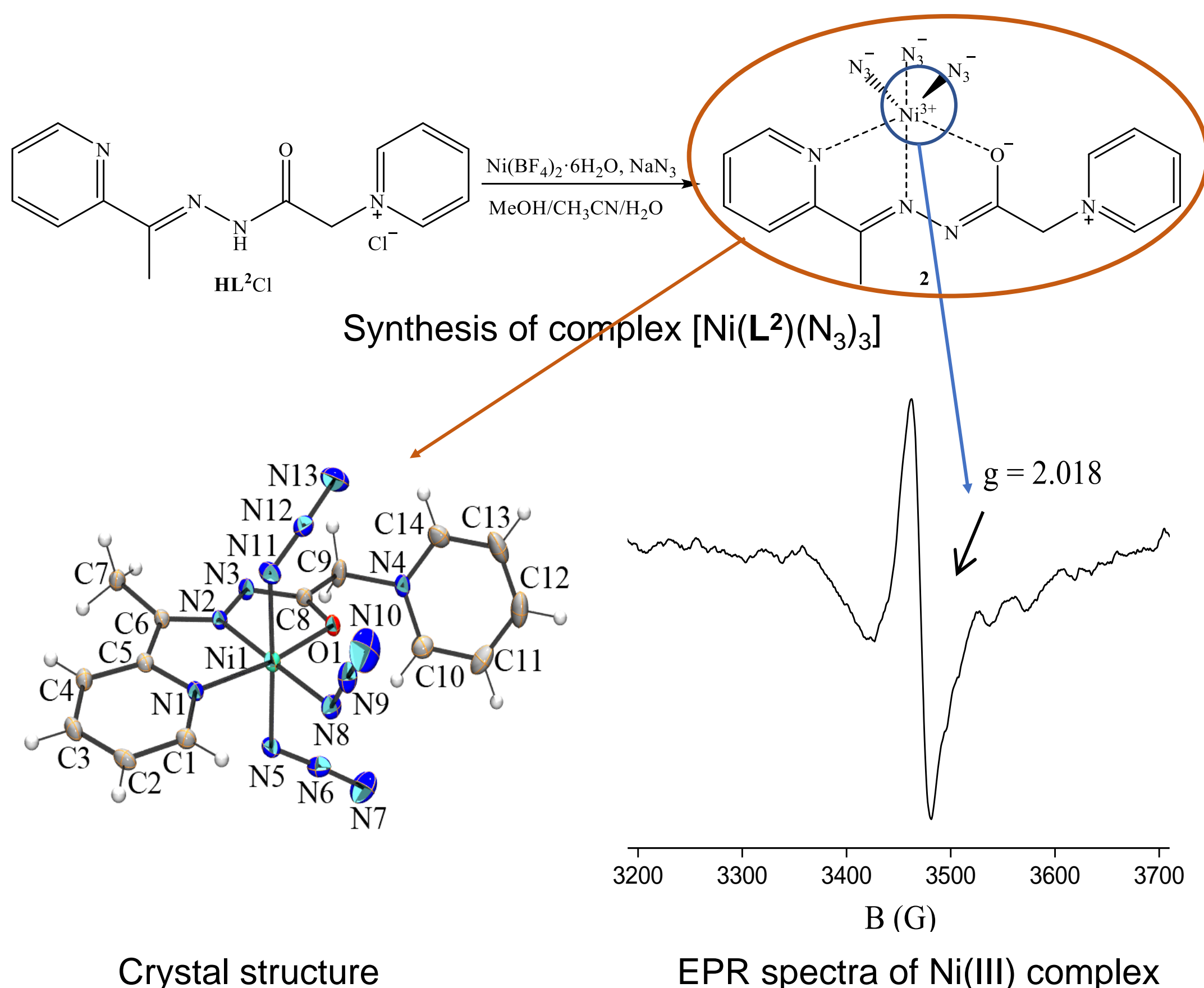
The conformational flexibility and large number of potential donor atoms of the hydrazone and thiosemicarbazone ligands allow different modes of coordination to metal ions. Depending on the reaction conditions and the nature of the metal, mono- or binuclear complexes can be formed. Hydrazone and thiosemicarbazone ligands can be coordinated in tridentate fashion mode to central metal ion, while vacant coordination sites can be occupied by same ligand or be filled by monodentate ligands.

Since Ni(III) is a relatively uncommon oxidation state for nickel, most previous research has examined the properties of Ni(II) complexes. This may also be explained by the fact that obtaining these complexes in the form of single crystals is practically impossible without adding an oxidizing agent or oxidizing properties of ligand itself.

Results and discussion

We report Ni(III) complex, $[\text{Ni}(\text{L}^2)(\text{N}_3)_3]$, formed by coordination of one hydrazone ligand coordinated through NNO donor set and three azide anions (HL^2Cl ligand, (*E*)-1-(2-oxo-2-(2-(1-pyridin-2-yl)ethylidene)hydrazinyl)ethyl)pyridin-1-ium chloride), complemented by DFT calculations.

To the best of our knowledge this is the first Ni(III) complex obtained under ambient conditions.



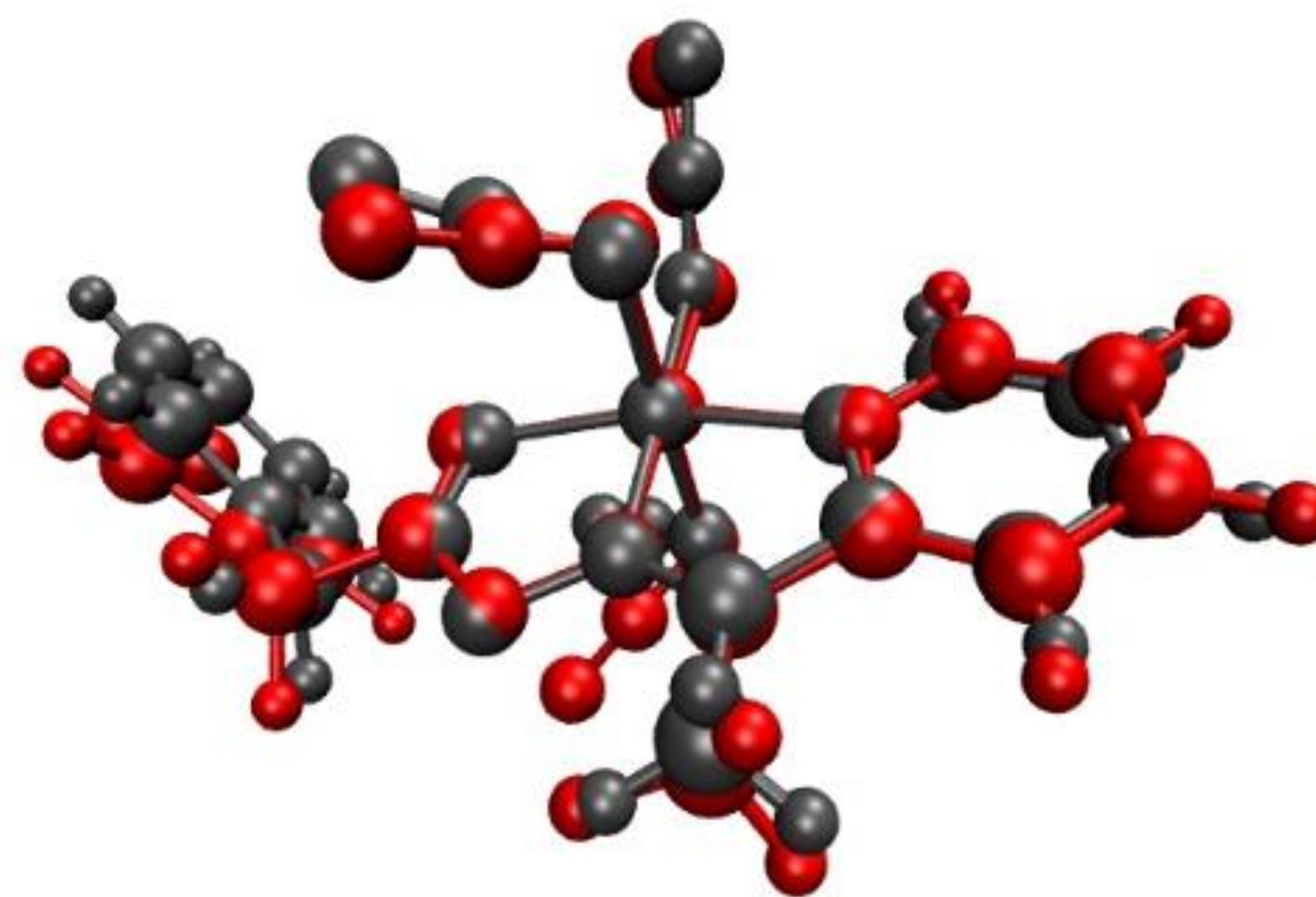
This unexpected result for the complex was finally confirmed by EPR spectroscopy.

The observed signal implies an unpaired electron consistent with a low spin ($S = 1/2$) Ni(III) electronic structure

DFT calculations

Density Functional Theory (DFT) calculations at the BP86-D3/def2TZVP level of theory revealed that optimization of the complex with Ni(II) as the central metal ion yielded a geometry with metal-ligand bonds that are on average 0.166 Å longer than those found in the crystal structure.

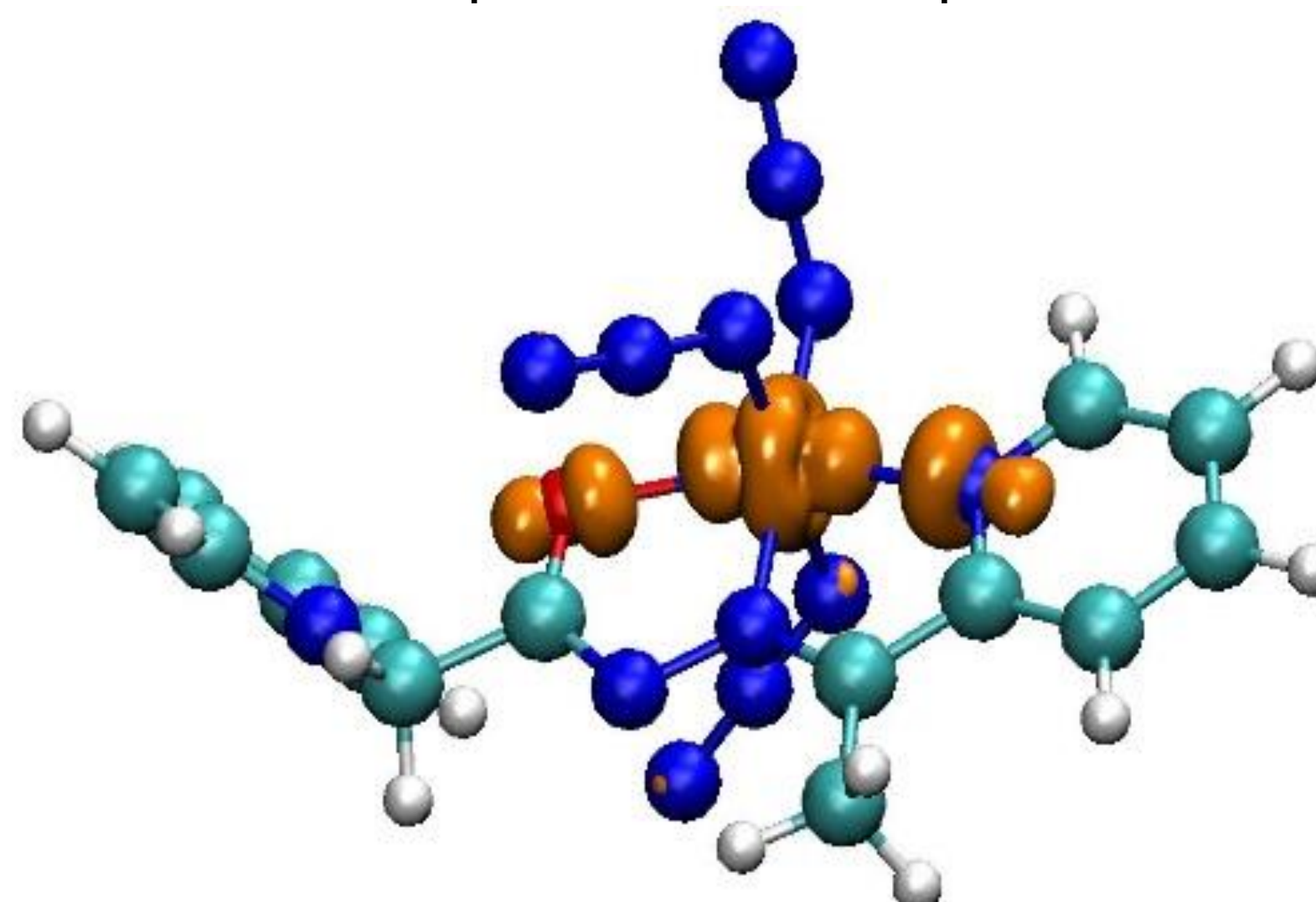
On the other hand, optimized geometry of the complex with low spin (doublet) Ni(III) central metal ion is much closer to crystal structure geometry. The main difference between crystal and DFT optimized structure is in the orientation of the azido ligands, probably due to involvement of azido ligands in intermolecular hydrogen bonding network found in the crystal structure of the complex.



Overlapped structures of the complex. Grey – crystal structure; Red – DFT optimized structure of low-spin Ni(III) complex.

Spin-state energies show that doublet state is the ground state for Ni(III) complex, with the quartet state higher in energy for 16.55 kcal/mol. This is in accordance with EPR data, which clearly indicates a doublet spin state in the solid state of complex.

Closer look at spin distribution, reveals that most of the spin density is located on Ni(III) (76.5%), and N(3) and O atoms (10.7% and 7.5%, respectively). Therefore, we concluded that the unpaired electron is almost completely located in the first coordination sphere of the complex.



Spin density distribution (orange isosurface with 0.004 $e^-/\text{Å}^3$ isovalue) in low-spin Ni(III) complex