Electronic structure of $(MePh_3P)_2[Ni^{II}(bdtCl_2)_2]$. $(CH_3)_2SO$ and $(MePh_3P)[Ni^{III}(bdtCl_2)_2]$, ($bdtCl_2$ - 3,6-dichlorobenzene-1,2-dithiolate)

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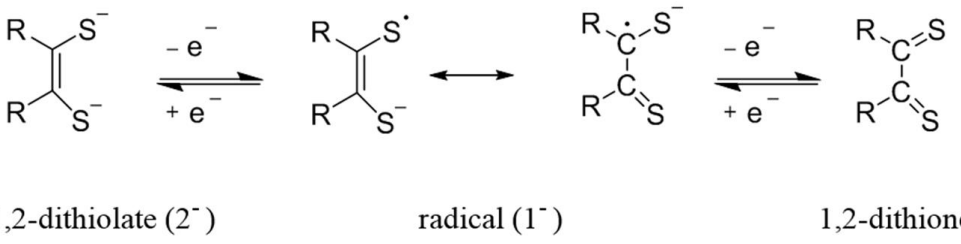
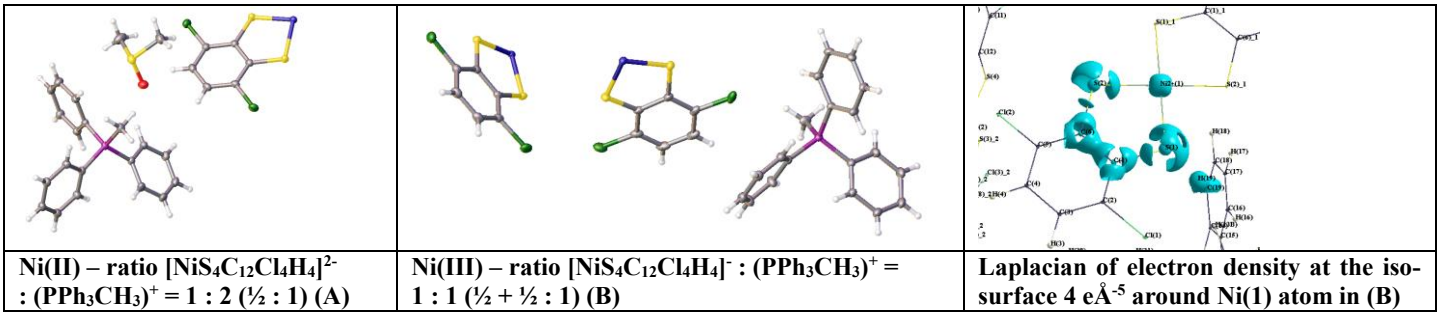
High-resolution X-ray diffraction experiments, theoretical calculations and atom-specific X-ray absorption experiments are applied to investigate two nickel complexes [Ni(II) (**A**) and Ni(III) (**B**)] (Figure 1a, 1b) with the non-innocent 3,6-dichlorobenzene-1,2-dithiolate ligand. Combining the techniques of metal K-, L-edge and sulphur K-edge X-ray absorption spectroscopy with high-resolution X-ray charge density studies, the experimental assessment of oxidation states of the central Ni atoms is studied and compared with theoretical predictions. Furthermore, the experimentally derived X-ray charge density (obtained via the multipole model) and the electron density from theoretical calculations are provided to further explore the contrast and contest of both approaches employed.





Ni(II) – ratio $[NiS_4C_{12}Cl_4H_4]^{2-}$: $(PPh_3CH_3)^+$ = 1 : 2 (½ : 1) (A)	**Ni(III) – ratio $[NiS_4C_{12}Cl_4H_4]^-$: $(PPh_3CH_3)^+$ = 1 : 1 (½ + ½ : 1) (B)**	**Laplacian of electron density at the iso-surface 4 eÅ^{-5} around Ni(1) atom in (B)**

Figure 1. Compounds(a) (A), (b) (B), (c) Laplacian of electron density The oxidation state of the central atom will be discussed [1] (Figure 1c).

[1] Machata, P., Herich, P., Lušpai K., Bučinský, L., Šoralová, S., Breza, M., Kožíšek, J. & Rapta, P. (2014). *Rev. Sci. Instrum.* **70**, 3554.

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