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Charge Density Study of two Ni(III) and Ni(II) complexes

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Experimental charge density of two nickel complexes with oxidation state +3 and +2 of composition (CH3(Ph)3P)+[Ni(bdtCl2)2]-, C31H22Cl4S4P1Ni1 [I] and (CH3(Ph)3P)+[Ni(bdtCl2)2]- dimethylsulfoxide solvate, C25H20Cl2S2P1Ni0.5; C2H6SO [II], (bdtCl2 = 3,6-dichloro-1,2-benzenedithiole), has been studied. The coordination of Ni central atom by bdtCl2 as a non-innocent ligand gives rise to interesting electronic properties. Compounds I and II crystalize in a monoclinic space groups P 21/c and II in P 21/n, respectively. Their coordination is square-planar with the chromophore [NiS4]. Obvious differences for interatomic distances in metallocycles were found. For I in Ni1-S1-C1-C6-S2-Ni1 there are bond lengths of 2.1534(1), 1.7375(5), 1.4144(8), 1.7327(5), 2.1432(1) Å; and in Ni2-S3-C7-C12-S4-Ni2 there are bond lengths of 2.1453(1), 1.7390(5), 1.4133(7), 1.7387(5), 2.1523(1) Å. For II in Ni1-S1-C1-C6-S2-Ni1 there are bond lengths of 2.1776(2), 1.7437(8), 1.4169(11), 1.7431(8), 2.1663(2) Å. Significantly longer distances for II are in good agreement with the lower oxidation state of central atom. Very accurate data for I an II complexes were obtained with Oxford Diffraction CCD GEMINI R diffractometer at 100K. Multipolar refinement and consecutive topological analysis was performed using XD package. Differences in distribution of electron density in both complexes will be disscussed and compared with quantum-chemical calculations at BP86/VTZP level of theory [1]. This work has been supported by Slovak Grant Agency APVV and VEGA (APVV-0202-10 and 1/0679/11).

[1] *P. Machata et al., Organometallics (submitted).*

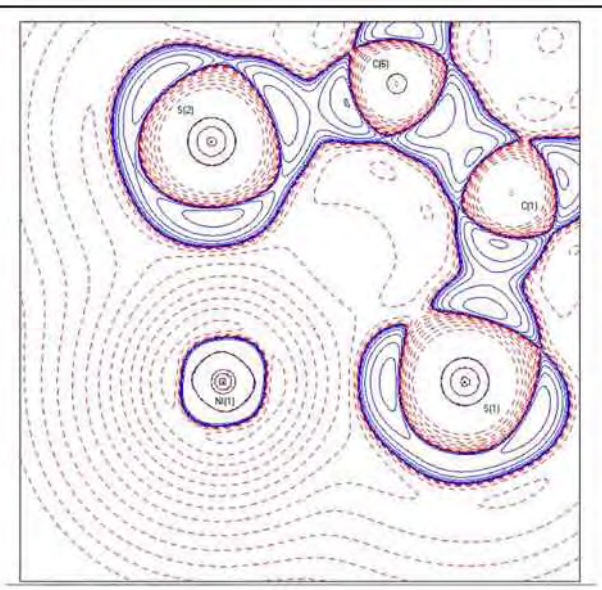

Fig. 1a. Laplacian distribution $L(\mathbf{r}) \approx \nabla^2 \rho(\mathbf{r})$ in the plane defined by atoms S(1) Ni(1) S(2) for **I**. Blue contours are positive, dashed red contours are negative.

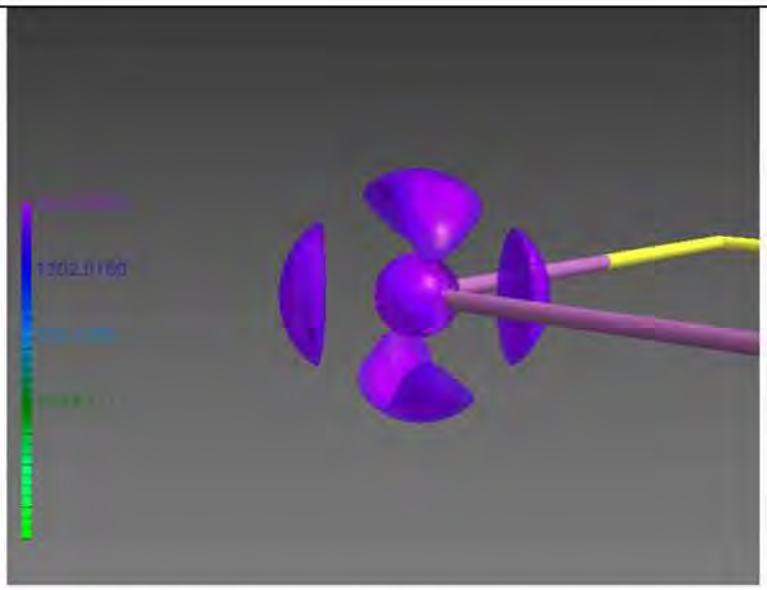

Fig. 1b. 3D-plots of the Laplacian of the electron density around Ni(1) at isosurface value of 1200 e Å^{-5} for **I**.

Keywords: charge density, Ni(III) complex, non-innocent ligand