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Experimental and theoretical studies of two new nickel(II)-based complexes containing the 2-methoxyethyl xanthate as a ligand

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Studies involving Ni(II)-containing complexes have gained prominence due to their potential applications in the fields of biology, industry, and catalysis.[1, 2] Keeping that in mind, this work describes the synthesis, spectroscopic characterization, and the crystal structure of two new Ni(II) complexes with 2-methoxyethyl xanthate ligand. Suitable single crystals of the complexes for X-ray diffraction studies were obtained through slow solvent diffusion (MeOH/EtOH). The crystal structure revealed neutral and anionic compounds with molecular formulas, $[Ni(S_2CO(CH_2)_2OCH_3)_2]$ **(1)** and $K[Ni(S_2CO(CH_2)_2OCH_3)_3]$ **(2)**, in which the xanthate ligand is coordinated to the nickel ion in a bidentate fashion, affording in a square-planar and octahedral distorted geometries (Figure 1a-b), respectively. For (2), S2CO(CH2)2OCH3 further fills the coordination sphere. In addition, theoretical thermodynamic analysis was performed at M06L/6-311++G**+LANL2DZ level, using Gaussian 09. This analysis showed that the neutral complex has a higher trend of formation than the anionic complex ($\Delta G_{NEUTRAL}$ = -55.01 and $\Delta G_{ANIONIC}$ = -15.86 kcal mol^{-1}) due to the higher repulsion between the ligands in the anionic complex, which causes a lower superposition energy between the M-L bond orbitals. These results were corroborated by the energy decomposition (EDA) and natural bond orbital analyses (NBO) (Figure 1c-d).

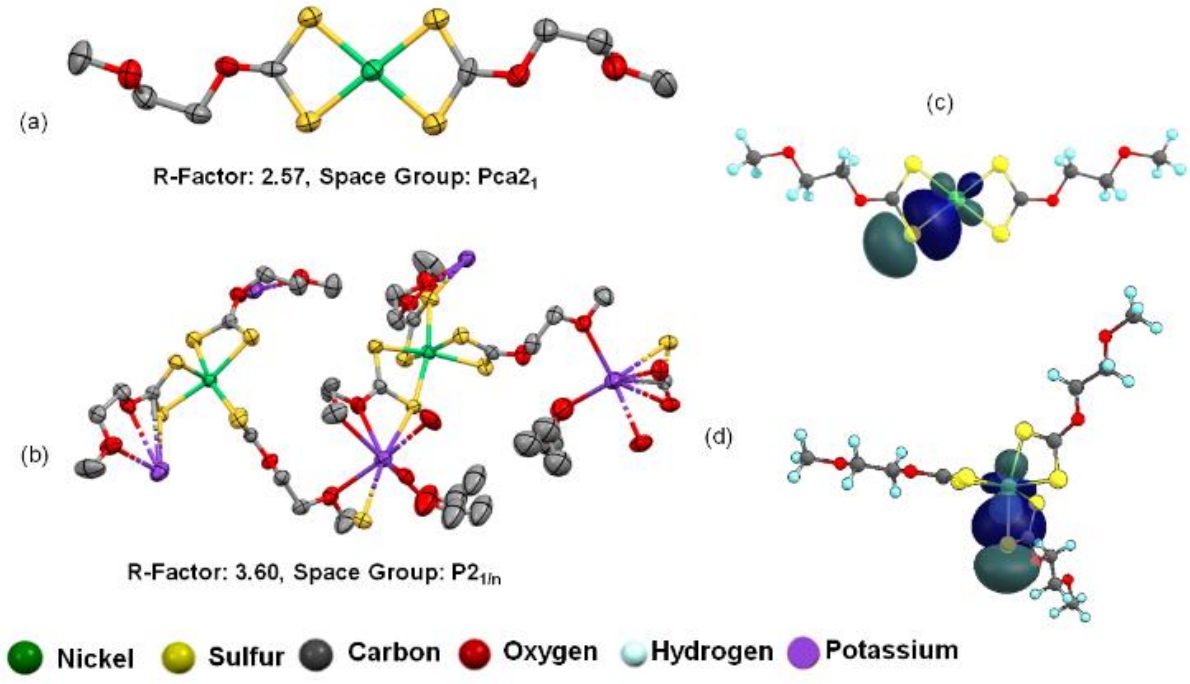

Figure 1. Crystal structures: **a)** $[Ni(S_2CO(CH_2)_2OCH_3)_2]$, **b)** $K[Ni(S_2CO(CH_2)_2OCH_3)_3]$ and NBO: **c)** square, **c)** octahedral

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References

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