

CHEMISORPTION OF EXCHANGE-COUPLED METAL COMPLEXES ON GOLD VIA AMBIDENTATE CARBOXYLATO LIGANDS

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A novel strategy for the fixation of redox-active dinickel(II) complexes with high-spin ground states to gold surfaces was developed. The dinickel(II) complex $[\text{Ni}_2\text{L}(\text{Cl})]\text{ClO}_4$ (where L represents a macrocyclic ligand) was reacted with ambidentate 4-(diphenylphosphino)benzoate (dppba) or 4-mercaptobenzoate (mba) coligands to form the carboxylato-bridged complexes $[\text{Ni}_2\text{L}(\text{dppba})]^+$ (**2**) and $[\text{Ni}_2\text{L}(\text{mba})]^+$ (**3**), which can both be isolated as perchlorate or tetraphenylborate salts. The auration of the complexes was probed on a molecular level, by reaction with AuCl or $[\text{AuCl}(\text{PPh}_3)]$, which leads to the monoaurated $\text{Ni}^{\text{II}}_2\text{Au}^{\text{I}}$ complexes $[\text{Ni}^{\text{II}}_2\text{L}(\text{dppba})\text{Au}^{\text{I}}\text{Cl}]\text{ClO}_4$ (**4**) and $[\text{Ni}^{\text{II}}_2\text{L}(\text{mba})\text{Au}^{\text{I}}\text{PPh}_3]^+$ (**5**), respectively. The bridging thiolate-functions of the N_6S_2 macrocycle are deeply buried and are unaffected/unreactive under these conditions. All complexes were fully characterized by ESI mass spectrometry, IR and UV/Vis spectroscopy, X-ray crystallography, cyclic voltammetry, SQUID magnetometry and HF-ESR spectroscopy. Temperature dependent magnetic susceptibility measurements reveal a ferromagnetic coupling between the two Ni(II) ions in **2-5** with J values ranging from 15 - 23 cm^{-1} . HF-ESR measurements yield a negative axial magnetic anisotropy ($D < 0$) which implies a bistable (easy axis) magnetic ground state. The binding of the $[\text{Ni}_2\text{L}(\text{dppba})]\text{ClO}_4$ complex to gold was ascertained by four complementary surface analytical methods: contact angle measurements, atomic force microscopy, X-ray photoelectron spectroscopy and spectroscopic ellipsometry. The results indicate that the complexes are attached to the Au surface via coordinative Au-P (or Au-S) bonds in a monolayer.

Keywords: Macrocyclic Ligands / High-Spin Molecules / Chemisorption / Ambidentate Phosphorus Ligands / Gold / Surface Complex

References

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