

Part 1: Experimental and theoretical studies of 2-cyano-2-isonitroso-N-piperidynylacetamide (HPiPCO), 2-cyano-2-isonitroso-N-morpholylacetamide (HMCO) and their Pt- and Pd-complexes.

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The reaction between substituted cyan-acetamides $\text{NC-CH}_2\text{-C(O)X}$ ($\text{X} = \text{N-piperidyne}$ or N-morpholyl residues) and gaseous methyl nitrite CH_3ONO in isopropanol at room temperature in the presence of a base within minutes leads to colorless cyanoximes 2-cyano-2-isonitroso-N-piperidynylacetamide (further as HPiPCO), and 2-cyano-2-isonitroso-N-morpholylacetamide (HMCO) in 70–90% yield. The deprotonation of HPiPCO and HMCO with a base such as NaOEt affords anionic Na-salts, bright-yellow in color originated from $n \rightarrow \pi^*$ transitions in the nitroso-chromophore. Anionic cyanoximates react with aqueous solutions of K_2MCl_4 ($\text{M} = \text{Pd}, \text{Pt}$) to form yellow-orange PdL_2 and dark blue-green polymeric $[\text{PtL}_2]_n$ ($\text{L} = \text{PiPCO}^-, \text{MCO}^-$), which upon treatment with DMSO or DMF breaks down to pale-yellow monomeric PtL_2 . Synthesized metal complexes were characterized by spectroscopic methods (IR, UV-Vis), measurement of the electric conductivity and the X-ray analysis. Both PdL_2 and PtL_2 exhibit non-electrolyte behavior in DMSO and DMF. Crystal structures of Pd(PiPCO)_2 and Pt(PiPCO)_2 were determined and revealed the formation of the *cis*-complexes with nearly planar geometry around the metal core and an adoption of the *cis-anti* configuration by anions, in contrast to the *trans-anti* geometry in structures of uncomplexed HPiPCO and HMCO. *Ab initio* calculations were performed for all six compounds: two cyanoxime ligands and four Pd and Pt metal complexes. A very satisfactory agreement between the calculated and experimental values of geometrical parameters of all evaluated compounds was attained. The electron densities, energies of HOMO and LUMO orbitals and molecular electrostatic potentials were calculated as well.

Słowa kluczowe

cyanoximes, synthesis, X-ray analysis, ab initio calculations

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