



Molybdenum complexes bearing the tris(1-pyrazolyl)methanesulfonate ligand: synthesis, characterization and electrochemical behaviour.

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Streszczenie

The tris(1-pyrazolyl)methanesulfonate lithium salt Li(Tpms) [$\text{Tpms} = \text{SO}_3\text{C}(\text{pz})_3^-$] reacts with $[\text{Mo}(\text{CO})_6]$ in NCMe heated at reflux to yield $\text{Li}[\text{Mo}(\text{Tpms})(\text{CO})_3]$ (**1**), which, upon crystallization from thf, forms the coordination polymer $[\text{Mo}(\text{Tpms})(\text{CO})_2(\mu\text{-CO})\text{Li}(\text{thf})_2]_n$ (**2**). Reaction of **1** with I_2 , HBF_4 or AgBF_4 yields $[\text{Mo}(\text{Tpms})\text{I}(\text{CO})_3]$ (**3**), $[\text{Mo}(\text{Tpms})\text{H}(\text{CO})_3]$ (**5**) or $[\text{Mo}(\text{Tpms})\text{O}_2]_2(\mu\text{-O})$ (**7**), respectively. The high-oxidation-state dinuclear complexes $[\{\text{Mo}(\text{Tpms})\text{O}(\mu\text{-O})\}_2]$ (**4**) and $[\{\text{Mo}(\text{tpms})\text{OCl}\}_2](\mu\text{-O})$ (**6**) are formed upon exposure to air of solutions of **3** and **5**, respectively. Compounds **1–7**, which appear to be the first tris(pyrazolyl)methanesulfonate complexes of molybdenum to be reported, were characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS, elemental analysis, cyclic voltammetry and, in the cases of Li(Tpms) and compounds **2**, **4**· $2\text{CH}_3\text{CN}$, **6**· 6CHCl_3 and **7**, by X-ray diffraction analyses. Li(Tpms) forms a 1D polymeric structure {i.e., $[\text{Li}(\text{tpms})]_n$ } with Tpms as a tetradentate N_2O_2 chelating ligand that bridges two Li cations with distorted tetrahedral coordination. Compound **2** is a 1D coordination polymer in which Tpms acts as a bridging tetradentate N_3O ligand and each $\text{Li}(\text{thf})_2^+$ moiety is coordinated by one bridging CO ligand and by the sulfonyl group of a contiguous monomeric unit. In **4**, **6** and **7**, the Tpms ligand is a tridentate chelator either in the NNO (in **4**) or in the NNN (in **6** and **7**) fashion. Complexes **1**, **3** and **5** exhibit, by cyclic voltammetry, a single-electron oxidation at oxidation potential values that indicate that the Tpms ligand has an electron-donor character weaker than that of cyclopentadienyl.

Słowa kluczowe

molybdenum, scorpionates, electrochemistry, solid state structures

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