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Exploring the Synthesis of New Dinuclear Cobalt Compounds with Valence Tautomerism Potential

Jamile R. Pavan, Carlos E. T. Bruzeguini, Thaís T. Fontana, Marcos A. Ribeiro,

Departamento de Química, Universidade Federal do Espírito Santo, Vitória, ES, Brazil
E-mail: marcos.a.ribeiro@ufes.br

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Systems capable of switching between two or more different electronic states as a result of external stimuli are of great interest for the development of materials with specific properties that can be used in the construction of molecular electronic devices.[1] In this context, systems that exhibit valence tautomerism (VT), a reversible intramolecular electron transfer phenomenon that occurs between metal centers and redox-active ligands, stand out as a particularly relevant category. Among these compounds, cobalt-*o*-dioxolene derivatives have been widely investigated, with electron transfer occurring from the catecholate ligand to the low spin cobalt(III) ion, forming a high spin cobalt(II) ion coordinated to a paramagnetic semiquinonate ligand.[2] This work sought to synthesize dinuclear cobalt compounds in order to obtain molecular systems that can alternate between three different electronic states, providing two-step VT.[3] To this end, in addition to the redox active ligand 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5`,6,6`-tetrol (spiroH_4), tetradentate nitrogen ligands N, N'-bis(2-pyridylmethyl)-1,2-diaminoethane (py$_2$en), N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane (1,3-py$_2$pn) and N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane (1,3-py$_2$pn) and N,N'-bis(2-pyridylmethyl)-1,2-diaminopropane (1,2-py$_2$pn) were used, which have not been previously employed in the construction of a valence tautomer. The three new compounds synthesized [{Co(py$_2$en)}$_2$(spiro)](BF$_4$)$_2$, [{Co(1,3-py$_2$pn)}$_2$(spiro)](BF$_4$)$_2$ and [{Co(1,2-py$_2$pn)}$_2$(spiro)](BF$_4$)$_2$ were characterized by infrared (IR), ultraviolet-visible (UV-vis) and electrical conductivity, and their results indicated that systems similar to the Co^{III}-spiro(cat^{2-}-cat^{2-})-Co^{III} form were obtained. Despite the low quality of the crystals obtained, X-ray diffraction measurements played a crucial role in determining the connectivity of the atoms and confirming the structures of the compounds designed. The synthesis of these systems opens up new possibilities for future research into the influence of new nitrogen ligands on catalysis and functional materials applications.

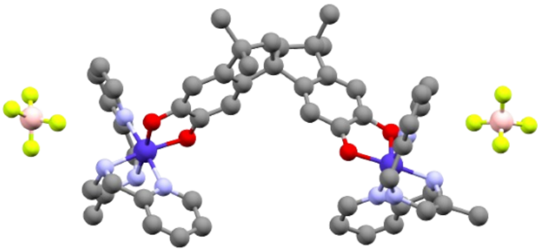

Figure 1. Structural representation of complex [{Co(1,2-py$_2$pn)}$_2$(spiro)](BF$_4$)$_2$. Color code: Co, dark blue; O, red; N, blue; C, gray; B, pink; F, yellow.

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