Magnetic properties of cobalt dioxolene complexes with tetradentate N-donor base

<u>Chegerev Maxim</u>,^{1*} Korchagin Denis,² Starikov Andrey,¹ Efimov Nikolay,³ Shilov Gennady,² Minkin Vladimir,¹ Aldoshin Sergey²

Investigation of metal complexes with redox-active ligands (*o*-benzoquinones and their imines) is one of the intensively developing fields of organometallic and coordination chemistry. Valence tautomerism (VT), also called redox-isomerism, is a unique phenomenon observed in metal coordination compounds, that involves a reversible intramolecular electron transfer between a metal center and a redox-active ligand (or ligands) caused by the action of temperature, pressure, irradiation, or electric field. Compounds capable of VT represent promising candidates for the design of molecular switches, photoresponsive devices or key substructures of molecular electronics and spintronics.

In this work a family of octahedral complexes $[(Me_2TPA)Co(36-Cat)]$ **1**, $[(Me_2TPA)Co(36-Cat)]PF_6$ **2** and $[(Me_2TPA)Co(diox-(OMe)_3)]BPh_4$ **3** $(Me_2TPA = bis(6-methyl-2-pyridyl)methyl)-(2-pyridylmethyl)amine; 36-Cat = dianion of 3,6-di-$ *tert* $-butylcatechol; diox-<math>(OMe)_3 - 2,5$ -di-*tert*-butyl-6-oxy-3,4,4-trimethoxy-cyclohexa-2,5-dienone) have been synthesized and their magnetic properties investigated. The neutral complex **1** was found to form a hexa- (CoO_2N_4) and pentacoordinated (CoO_2N_3) isomers, possessing different structure and magnetic behavior. One electron oxidation of **1** gives rise the ionic complex **2**, demonstrating thermally induced VT transition $(L_SCo^{II}-Cat \rightarrow {}_{HS}Co^{I}-SQ)$ in the solid state. An aerial oxidation of **1** results in the formation of ionic complex of ${}_{HS}Co^{II}$ bearing cyclohexadienonate ligand - **3**. Compounds **1** and **3** were found to demonstrate slow magnetic relaxation at applied fields of 1500-2500 Oe.

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¹ Institute of Physical and Organic Chemistry, Southern Federal University, Stachki Avenue, 194/2, 344090, Rostov-on-Don, Russia

² Institute of Problems of Chemical Physics of RAS, acad. Semenov Av., 1, 142432 Chernogolovka, Russia

³ Kurnakov Institute of General and Inorganic Chemistry of RAS, Leninsky avenue, 31, 119991, Moscow, Russia *E-mail: mchegerev@sfedu.ru