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Low-dimensional (0-D and 1-D) molecular magnets are the molecules made of an organic and metal constituents that behave as magnets at molecular level. 0-dimensional magnets are the polynuclear coordination compounds called now as Single-Molecule Magnets. 1-D chain coordination polymers are named as Single-Chain Magnets. The magnetism of these objects is fundamentally different from the conventional magnets. Indeed, such molecules exhibit “quantum properties” and display slow relaxation of magnetisation. This attracted much attention as they open a way for extra miniaturization with perspective application in information storage and processing. The objectives of the current project were to continue a research performed within the framework of incoming phase (PIIF-GA-2011-301689), namely the study of employment of orbitally-degenerate 4d or 5d (Ru, Os and Re) metal complexes for their assembling in polynuclear complexes with 3d metal complexes with the aim to obtain the materials possessing slow dynamic of magnetization.

An essential part of the work performed during the year was devoted to the synthesis of the precursors since earlier prepared osmium and rhenium containing starting materials were consumed throughout the incoming phase. It should be specially underlined that in carrying out this seemingly routine work the new more effective synthetic protocols were elaborated for the variety of the 4d and 5d cyanometallates. They have been prepared as the salts with different organic cations, some of them having been prepared for the first time. Among them a tris-tetrabutylammonium osmium heptacyanide, a unique example of seven coordinated homoleptic complex of osmium. The results of this research was summarized in the chapter “Homoleptic Osmium cyanide complexes: synthesis and perspective application in molecular magnetism” in the book “Osmium: Synthesis, Characterization and Applications“, Ed: G. Wise, Nova Science Publishers, NY, 2015 (www.novapublishers.com/catalog/product_info.php?products_id=55752).

We also synthesized several new heterobimetallic assemblies of 5d (osmium and rhenium) metal centers and 3d metal ions as well as the polynuclear complexes involving 3d metal ions and stable nitroxide radicals. The majority of these new compounds have been structurally characterized by single crystal X-ray diffraction analysis and their magnetic properties have been investigated in static and dynamic regimes. Publication of the result is under submission to international reviews.

One of the important achievements are the synthesis and characterization of a new bridging paramagnetic organic ligand and their binuclear complexes of 3d metal ions, a compound incorporating Co(II) was found to be SMM at applied field of 1000 Oe. Another high spin biradical containing molecular building block $[\text{Ni}(\text{BiRad})]^{2+}$ has been investigated and probed as NMR thermosensor, a manuscript devoted to this research (“Nikel(II) Complex of Bis-(Imino Nitroxide): Structure, Magnetic Properties and Paramagnetic Probe Behavior in NMR Spectroscopic Studies of Fast Molecular Conformational Dynamics and Temperature Control”) having been submitted to “Inorganic Chemistry”.

We were able to prepare a series of binuclear involving bridging 2-PmNN ligand. As a template matrix hexafluoroacetylacetonates of 3d metals (Cu^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+}) were used. A molecular structure of Co complex is shown in Fig. 4. The magnetic measurements were made for all four compounds. It was found that Co-dimer is field-induced SMM (Fig. 6). It is the first example of the SMM among the Co-dimers with NN bridge

We have made also a complex involving a biradical bridge, $[\text{Co}(\text{hfac})_2-\mu-(\text{BisNN})\text{Co}(\text{hfac})_2]$. This is a congener of $[\text{Co}(\text{hfac})_2-\mu-(2\text{-PmNN})\text{Co}(\text{hfac})_2]$ dimer. This biradical containing two nitronyl nitroxides was known earlier but binuclear specie was known only for $\text{Mn}(\text{hfac})_2$ and $(\text{Ni}(\text{hfac})_2)$ matrix. We were able to obtain their Co relative $[\text{Co}(\text{hfac})_2-\mu-(\text{BisNN})\text{Co}(\text{hfac})_2]$ and to resolve its crystal structure (Fig.5). In near future we plan to prepare and to study the polymer complexes involving the bridging radicals and 3d metal ions. The preliminary results were presented at *The 7th International Conference on Nitroxide Radicals (SPIN-2014)*, Sept. 14-20, 2014, Kaliningrad, Russia. We need in few additional studies to finish a manuscript to be submitted in the journal with high Impact Factor.

Results have multidisciplinary significance, contributing to areas including molecule-based materials, chemistry and nanotechnology. Perhaps the most immediate tangible impact will be on information

processing, contributing to European leadership in a booming technology sector and strengthening of the collaborative research contacts between Russia and EC.

As it was demonstrated during the incoming phase three bimetallic assemblies $(\text{CAT})_2[\text{Mn}(\text{acacen})][\text{M}(\text{CN})_6]$ $\text{M}=\text{Fe}$ for $\text{CAT}=\text{Et}_4\text{N}^+$, Ph_4P^+ , and $\text{M}=\text{Os}$ for $\text{CAT}=\text{Ph}_4\text{P}^+$ display a slow relaxation of magnetization and hysteresis below 4 K (Fig.2). During the return phase we have continued the research in this direction and have obtained two neutral bimetallic 1-D polymers involving hexa-cyanometallates of Ru(III) and Os(III), and isomorphous to previously reported SCMs $[\text{Mn}^{\text{III}}(\text{SB}^{2+})\text{M}^{\text{III}}(\text{CN})_6]$ (SB^{2+} =doubly charged four dentate ligand) 3d $\text{M}(\text{III})=\text{Fe}, \text{Mn}, \text{Cr}$ [Miyasaka H. et al *Chem. Eur. J.* 2012, 18, 3942]. We have analyzed magnetic properties and SCM behavior of $[\text{Mn}^{\text{III}}(\text{SB}^{2+})\text{M}^{\text{III}}(\text{CN})_6]$, $\text{M}=\text{Ru}, \text{Os}$ compared to those for the anionic chain $(\text{Ph}_4\text{P})_2[\text{Mn}(\text{acacen})\text{Os}(\text{CN})_6]$ [E.V. Peresyphkina, A.M. Majcher, M. Rams, K.E. Vostrikova *Chem. Commun.*, 2014, 50, 7150-7153]. It was shown that the $[-\text{Mn}^{\text{III}}-\text{NC}-(\text{Ru}^{\text{III}}/\text{Os}^{\text{III}})-\text{CN}-]$ chain represents a novel class of SCMs, in which magnetic anisotropy originated from a complicated interplay of single-ion ZFS anisotropy of Mn^{III} centers and unusual, highly anisotropic spin coupling between $(\text{Ru}/\text{Os})^{\text{III}}$ and Mn^{III} centers. This interaction is described by a three-axis spin Hamiltonian with opposite sign of anisotropic exchange parameters (namely, with antiferromagnetic J_x and J_z and ferromagnetic J_y) and with non-collinear orientation of the local magnetic axes x , y , and z . We demonstrate that their unusual magnetic behavior results from a complicated interplay of $\text{Mn}-\text{Ru}(\text{Os})$ anisotropic spin coupling and ZFS effect of Mn^{III} ions. A theoretical model of anisotropic spin coupling between orbitally-degenerate $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ complexes and attached Mn^{III} ions is developing and specific microscopic mechanisms of highly anisotropic spin coupling in $\text{Mn}^{\text{III}}-\text{NC}-(\text{Ru}/\text{Os})^{\text{III}}$ linkages will be analyzed in detail. *A report based on these results was presented at the Nikolaev's Conference-contest, NIIC, 24-25 Dec 2014, Novosibirsk, Russia as well as a full paper is in preparation.*

The studies we have performed belong to basic research but it aims to not only future applications in the field of information processes but also affords to the physicists to elaborate new theoretical models describing slow magnetic dynamics. Indeed, SMM have been proven to be relevant for applications in quantum computing and may satisfy the societal demand for mass data mining. Our researches were multidisciplinary and our result interest the all field of molecular based materials, inorganic and physical chemistry as well as nanotechnology. Our results promote synergy and added value in the field of chemistry and establish a foundation for high-quality research.

Quantum molecular nano-magnets could lead to high-density information storage based on spin flips in single molecules. Scientists developed new magnetic materials rationally designed to overcome current bottlenecks to widespread implementation.

Results have multidisciplinary significance, contributing to areas including molecule-based materials, chemistry and nanotechnology. Perhaps the most immediate tangible impact will be on information processing, contributing to European leadership in a booming technology sector.