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Modern Studies in the Area of Molecular Magnets: State, Problems, and Prospects

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Abstract—The review considers the theoretical foundations and some recent results of investigations of the specific class of magnetically active materials: molecular magnets (single-molecule magnets) and molecular magnets with the linear chain structure (single-chain magnets). Possibilities and promising approaches to controlling their magnetic properties are analyzed.

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Unswerving increase in scientific interest in nanosized magnetic materials is due to the modern technological break-through in the area of development of hyperfast supercomputers and devices for recording, storage, and reproduction of high-density data leading to drastic changes in the field of information technologies [1–3]. An important landmark of similar studies is the discovery of the so-called molecular magnets (single-molecule magnets, SMM) in which the classical phenomenon of residual magnetization retention is based on magnetic anisotropy at the molecular and atomic levels [4–6]. Similar systems make it possible to develop basically new devices for spintronics and molecular electronics [7–11] but also provide unique possibilities for studying quantum magnetic effects, for example, magnetization tunneling [12–14]. The studies of molecule magnets were primarily concentrated on coordination compounds of 3*d* metals [15–22]. However, to the present time derivatives of rare-earth elements and even 5*f* ions attract rapt attention of researchers due to their substantial magnetic anisotropy, which is a necessary condition for the appearance of the SMM properties. The discovery of the ability to retain residual magnetization in mononuclear rare-earth metal complexes or mixed polynuclear complexes (3*d*–4*f* ions) evoked the second wave in studying molecule magnets [23–28]. At the same time, it should be mentioned that the wide application of technologies using SMM is possible only upon the cardinal solution of two main problems. The first problem is that the unique properties of molecule magnets are manifested only in the range of superlow temperatures. Therefore, either such a region of application where this temperature criterion would be insubstantial will be revealed in future, or the effective temperature range will be increased. The second problem is related to the solution of questions of SMM immobilization on technological surfaces without changing the physicochemical properties of molecular magnets. It should be mentioned that there are only few examples for the successful solution of this problem.

Molecular magnets as directions of growth and development. Wide series of similar derivatives named "Mn_{12} archetype" [30] and homopolynuclear compounds of other transition metals of the first row [31–38] have been synthesized since the discovery of the SMM properties in the dodecanuclear mixed-valence manganese complex $[M_{12}O_{12}(CH_3COO)_{16}(OH)_4]$ [4, 29] with the total spin of the ground state $S = 10$. Before 2007, compounds of the "Mn_{12}" group were SMM with the highest values of the blocking temperature ($T_B \approx 3.5$ K) and anisotropic barrier (up to 74 K). To the present time, these are derivatives containing the cluster core Mn_6 ($T_B \approx 4.5$ K, anisotropic barrier ~86.4 K) [20, 39, 40]. As known [6], the main requirements to the appearance of the SMM properties in a coordination compound are the high spin of the ground state of the cluster (S) and the negative sign of the spin-orbital interaction parameter (D) reflecting the internal magnetic anisotropy of the paramagnetic center, and the above indicated anisotropic barrier is determined as $U_{eff} \approx |D|S^2$ [41]. Substantial progress in studying molecule magnets was achieved in respect of increasing parameter S, whereas the synthetic possibilities of the variation of the absolute value of parameter D are fairly restricted [42, 43]. The question whether a combined accomplishment of high values of the total spin of the ground state and the spin-orbital interaction parameter remains disputable [44]. It was shown that a significant spin of the ground state can be attained in the coordination compounds of 3*d*–4*f* metals, unlike the homonuclear 4*f*-metal derivatives, since a significant ferromagnetic exchange compara-

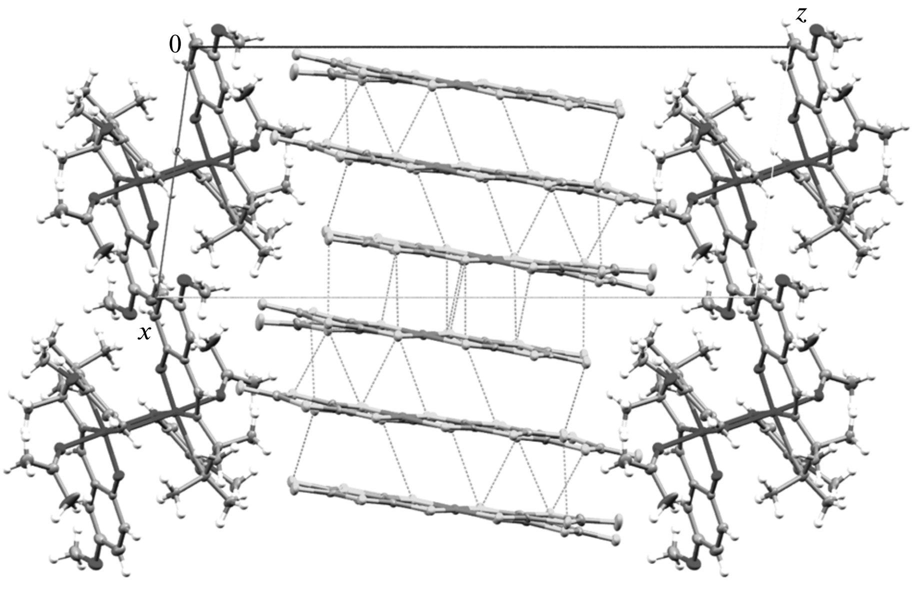

Fig. 1. Structure of complex **I**. The distances between the sulfur atoms that are shorter than the sum of the van der Waals radii (3.7 Å) are designated by dashed lines [45].

ble with the magnetic exchange in the polynuclear 3*d* complexes is observed in these systems.

The possibilities of formation of the so-called hybrid materials combining the semiconducting properties and the SMM properties were shown [45]. The main method for the preparation of similar systems is the combination of individual components that possess magnetically active and conducting properties by molecular self-assembling [46–49]. In the cited work, this "hybrid" was obtained by the electrochemical oxidation of an acetone solution of two coordination compounds: $(Mn^{III}(5\text{-MeOsaltmen})(H_2O))_2(PF_6)_2$, where 5-MeOsaltmen is *N*,*N*-(1,1,2,2-tetramethylethylene)bis(5-methoxysalicylidenediaminate), and $(NBu_4)[Ni(Dmit)_2]$ (Dmit is 2-thioxo-1,3-dithiol-4,5-dithiolate). The formed complex has the composition $[Mn(5\text{-MeOSaltmen})(acetone)]_2[Ni(Dmit)_2]_6$ (**I**) in which the $[Mn_2]$ core is characterized by the SMM properties with the total spin of the ground state $S = 4$ and is organized into the layered structure presented in Fig. 1.

As mentioned [45], the π–π interaction between individual layers including the coordinated Ni^{2+} ions results in the paramagnetism of the latter, which, in turn, transforms the magnetochemical behavior of complex **I** compared to the structurally similar derivative $[Mn(5\text{-MeOSaltmen})(acetone)]_2[Ni(Dmit_2]_7$ [50] that differs by the ratio of "hybrid-forming" components. Although an attempt to obtain a compound with electron superconductivity (the decribed complex behaves as a semiconductor) was unsuccessful [45], the data presented [45] unambiguously prove that the properties of the SMM can be controlled when combining the molecule magnets and molecules of coordination compounds with electron conductivity (complex $[Ni(Dmit)_2]$).

The work [51] is devoted to the study of one more important physicochemical property of molecular nanomagnets: magnetocaloric effect [52–56]. This property is associated with the principal application of the SMM as cooling devices that make it possible to attain superlow working temperatures. The authors [51] succeeded to join Ni^{2+}, Co^{2+}, and Co^{3+} ions with Gd^{3+} and Dy^{3+} ions to obtain supramolecular cores $Ln_{42}M_{10}$ ($Ln = Gd^{3+}, Dy^{3+}$; $M = Co^{2+}, Co^{3+}, Ni^{2+}$). It was experimentally proved that the combination in one molecule of the magnetically isotropic Gd^{3+} ion or magnetically anisotropic Dy^{3+} ion with transition metal ions is a key to the appearance of the presently highest (among the 3*d*–4*f* complexes) magnetocaloric effect with the simultaneous manifestation of the SMM properties by the Dy^{3+} derivative. In addition, it was shown that supramolecular architectures of complexes of the mixed 3*d*–4*f* type can be built using small (by structural characteristics) molecules of organic ligands and the directed variation of binding anions.

Wide recent studies of the dynamics of the magnetization relaxation in the SMM established an interesting phenomenon of the stepped character of this characteristic of molecule magnets. For example, it is shown that some lanthanide-based SMM exhibit two states of magnetic relaxation [57–59]. A similar situation is characteristic of the SMM based on the uranium complex $U_2(BPz)_6$ (BPzis dihydrobis(pyrazolyl)borate) [60]. Even the chain (1D) oxalate-bridged heteronuclear Cu–Co complexes also manifest two relaxation regions at different temperatures [61]. An interesting example of a similar type of sys-

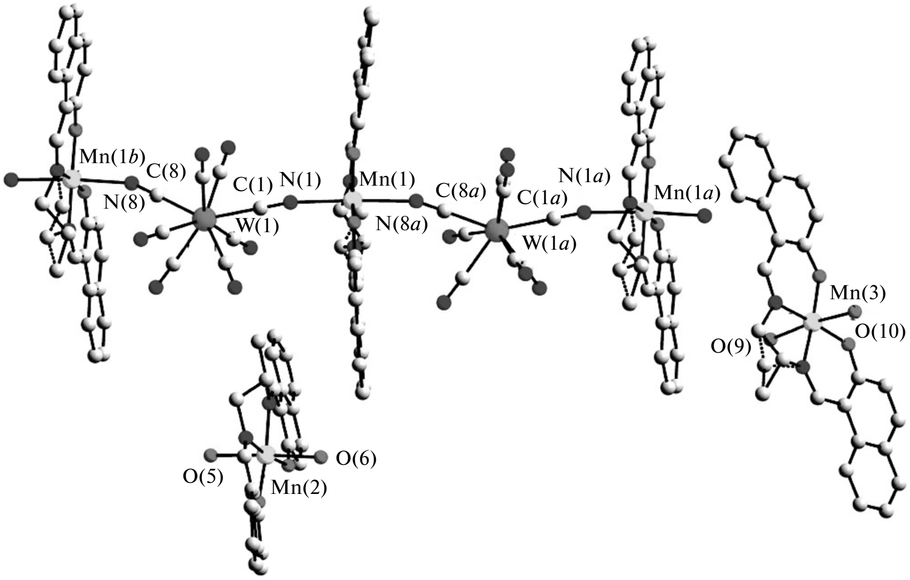

Fig. 2. Structure of complex **II** [62].

tems is presented in the work [62] devoted to the synthesis, structural studies, and magnetic properties of the 1D polynuclear complex $[Mn(L)W(CN)_8][Mn(L)(H_2O)_2]_2 \cdot MeCN \cdot H_2O$ (**II**) (H_2L is *N*,*N*-bis(2-hydroxynapthalidene-1-carbaldehydene)-1,3-diaminopropane) including heteronuclear anionic chains W^VMn^{III} and isolated cations Mn^{3+} (Fig. 2).

Complex **II** obtained by the reaction of stoichiometric amounts of $Cs_3[W(CN)_8] \cdot 2H_2O$ and the corresponding Mn^{3+} complex with the indicated Schiff base is a 1D bimetallic chain polymer built of the $Mn^{III}W^V$ fragments bound by the cyanide bridges and two crystallographically different Mn^{III} complexes with the Schiff base (Fig. 2). The two-stepped character of the magnetic relaxation of this compound is explained by both the magnetic interaction in the framework of the polynuclear chain and the three-dimensional magnetic ordering at superlow temperatures.

It should be mentioned that the heating of complex **II** to 40°C accompanied by the removal of H_2O molecules results in the loss of the SMM properties by the obtained dehydrated derivative. This fact clearly proves the possibility of controlling the character of the magnetic properties of the polynuclear complexes and simultaneously indicates the determining influence of details of the fine structure of the complex on the possibility of manifestation of the SMM properties, which is confirmed by the experimental data [63]. In this work, a new polynuclear manganese(II,III) complex (**IIIa**) was studied. Complex **IIIa** was formed of the starting clusters **III** as "building" blocks by the synthesis of the supramolecular chain involving azide and oximate groups as binding units (Fig. 3). The polynuclear chains in complex **III** are reliably isolated from each other (Fig. 3b) due to which the magnetic exchange of the ferromagnetic character between the manganese ions is observed only inside the chain. The authors note that this complex has a very low blocking temperature (lower than 2 K) in spite of the ferromagnetic exchange interaction that usually favors the SMM properties of the compound. This circumstance is explained by the unfavorable anisotropic factors, which, as already mentioned, along with the formation of the maximum spin of the ground state is the most important condition for the formation of molecule magnets [64–66].

The preparation of molecule magnets on the basis of rare-earth metal complexes seems to be very promising due to the high local anisotropy of lanthanide ions [67]. In similar systems the exchange interaction between 4*f* and 3*d* ions does not always result in more pronounced SMM properties, which is indicated by the published results [68].

Using the polydentate ligand system presented in Fig. 4, the authors [68] obtained both the Dy^{3+} mononuclear complex (**IV**) and the heteronuclear derivative with two additionally coordinated Mn^{3+} ions (**V**) (Fig. 5). The magnetic properties of mononuclear complex **IV** correspond to the very weak intermolecular antiferromagnetic interaction between the Dy^{3+} ions, whereas complex **V** is characterized by the intramolecular ferromagnetic exchange between the Mn^{2+} and Dy^{3+} ions.

The authors [68] showed that, unlike the mononuclear complex manifesting the SMM properties, the heteronuclear 3*d*–4*f* derivative has no these properties. In authors' opinion, the "switching off" of the SMM properties in the heteronuclear derivative is caused by the exchange interaction between the Mn^{3+}

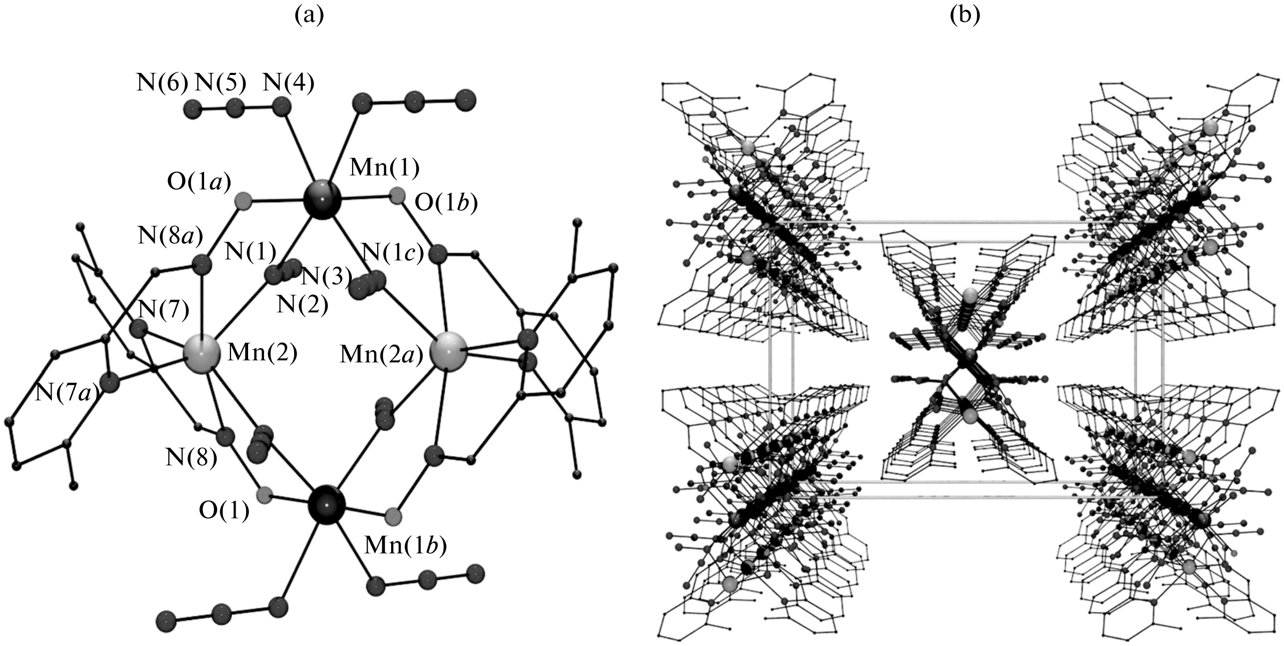

Fig. 3. Molecular structures of (a) complex **III** and (b) the chain of tetranuclear molecules bound by azide bridges in the crystalline complex [63].

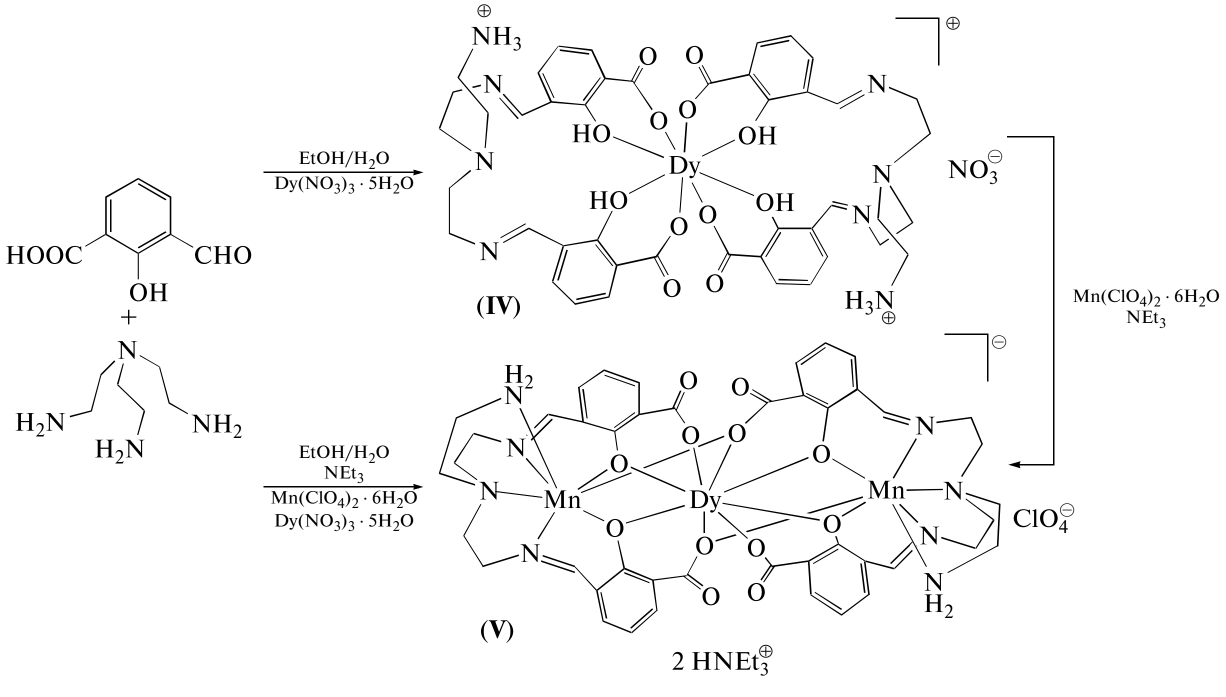

Fig. 4. Scheme of the syntheses of complexes **IV** and **V** [68].

and Dy^{3+} ions, and its energy is lower than the value of the energy barrier characterizing the bistability of the mononuclear complex. The "random" magnetic field formed due to the magnetic exchange interaction intensifies the effect of quantum magnetization tunneling, which the main reason for the disappearance of the SMM properties. Therefore, the authors [68] draw a very important conclusion that the potential ferromagnetic exchange between the transition metal and lanthanide ions should be fairly high to manifest pro-

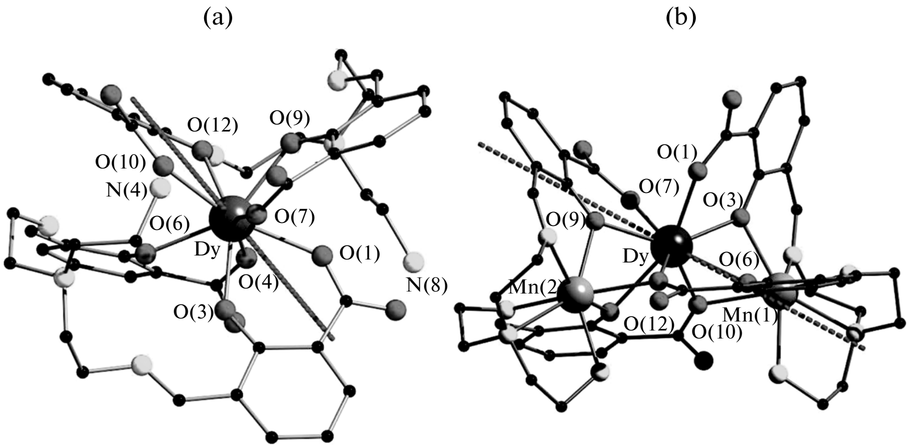

Fig. 5. Structures of complexes (a) **IV** and (b) **V**. Dashed line shows the orientation of the principal axis magnetic anisotropy of the Dy^{3+} ion [68].

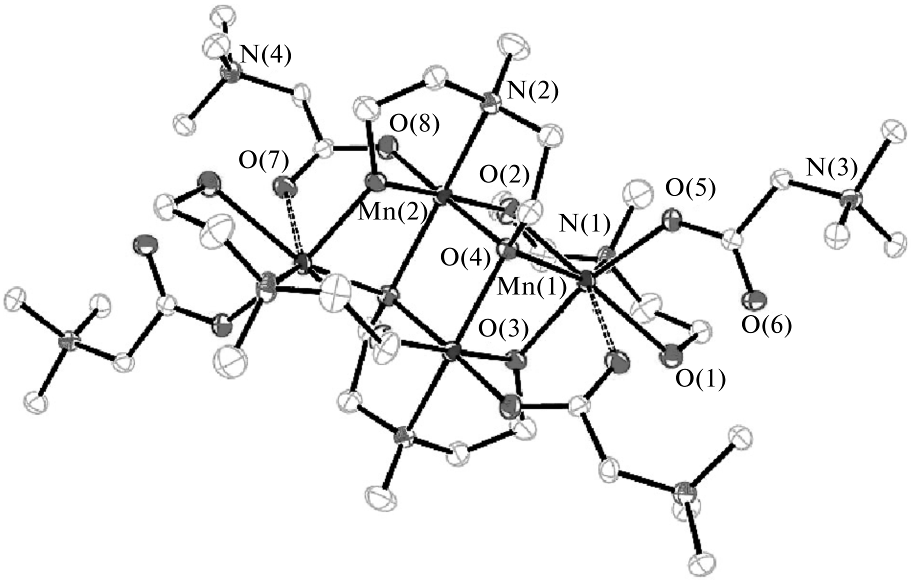

Fig. 6. Structure of complex **VI** [75].

nounced SMM properties in the heteronuclear 3*d*–4*f* systems [69]. The experimental approaches to the solution of the stated problem are described in the works cited below, and the results presented in [70–73] form their theoretical basis.

As known, the quantum effects of molecular magnetism are very sensitive to specific features of the crystal packing [74] and, hence, rather bulky ligand systems, glycine-betaine and *N*-methyldiethanolamine, were used [75] for the synthesis of coordination compounds containing the Mn_4 core (**VI**) with the SMM properties (Fig. 6). These ligand systems provide a reliable isolation of individual 2D layers of the coordination compounds (Fig. 7), which substantially decreases the probability of the magnetic exchange between the layers. The latter circumstance is considered [75] to be important for the detailed analysis of the phenomenon of magnetic hysteresis of single crystals, which, in turn, allows a deeper examination of the quantum tunneling effects of molecule magnets.

It was shown [76] that structurally similar ligand systems, tris(pyrazolyl)borates, can be used for the formation of a certain symmetry of the molecular complexes optimum for the appearance of the SMM

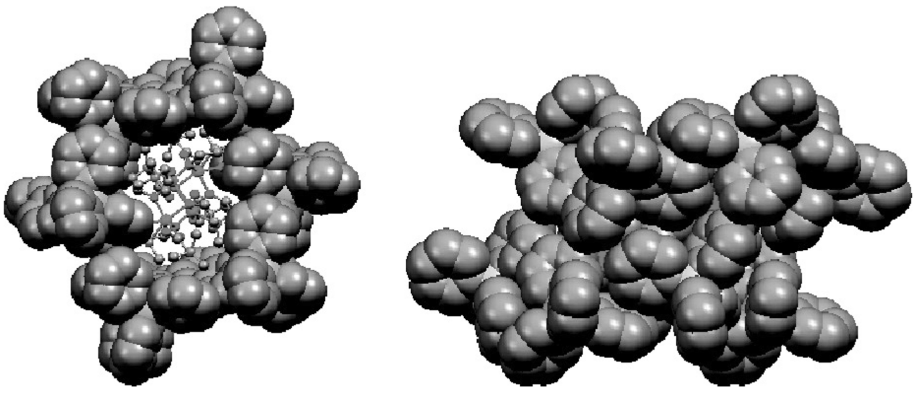

Fig. 7. Magnetic isolation of individual 2D layers in coordination compounds of the **VI** type [75].

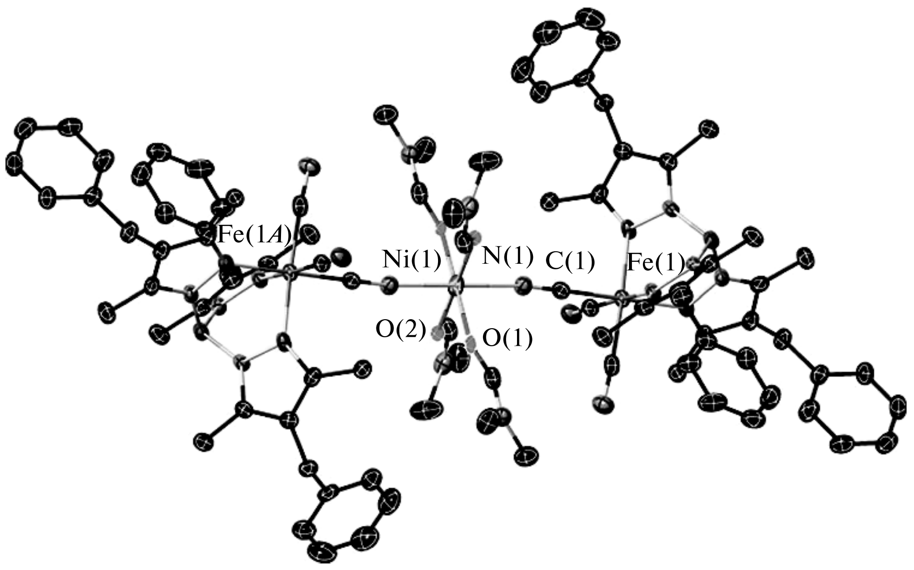

Fig. 8. Structure of complex **VII** [76].

properties. The authors note that the treatment of the cyanide metal complexes with these ligands can afford polynuclear derivatives with the possibility of structural tuning at the molecular level [77–79]. The reaction of $[\mathrm{Net_4}](\mathrm{Tp})\mathrm{Fe^{III}(CN)_3}] \cdot \mathrm{H_2O} \cdot \mathrm{MeOH}$ (Tp is tris(3,5-dimethyl-4-benzyl)pyrazolyl borate) with $\mathrm{Ni^{II}(OTf)_2}$ (Otf is trifluoromethanesulfonate) in dimethylformamide in a ratio of 2 : 1 yielded the heterotrinuclear linear complex $\{(\mathrm{Tp})\mathrm{Fe^{III}(CN)_3}]_2[\mathrm{Ni^{II}(DMF)_4}]\} \cdot 2\mathrm{DMF}$ (**VII**), whose structure is shown in Fig. 8.

Complex **VII** is characterized by the ferromagnetic exchange in the three-center chain ($J/K_B = +7.1$ K) with the total spin of the ground state $S = 2$. The authors believe that, similarly to analogous cyanide $\mathrm{Fe^{3+}/Ni^{2+}}$ derivatives containing the complex fragment $[(\mathrm{TpR})\mathrm{Fe^{III}(CN)_3}]^-$ [80, 81], the nonzero spin of the ground state and "favorable equalization" of the anisotropy axes of the ions results in the appearance of the SMM properties in these complexes.

The important topic developed recently toward studies of molecule magnets is devoted to the investigation of the appearance of these properties only in mononuclear coordination compounds. Similar studies include the work [82] studying the influence of the ligand substitution effect on structural distortions of the coordination node of the $\mathrm{Co^{2+}}$ complex (**VIII**) inducing changes in the spin-orbital interaction parameters of the metal ion (Fig. 9). The influence of substituents R appears as a shift of the $\mathrm{Co^{2+}}$ ion in the complex with R = Ph compared to that with R = $\mathrm{CH_3}$ from the plane of the coordination node toward the axially coordinated $\mathrm{NCS^-}$ ion by 0.52 Å.

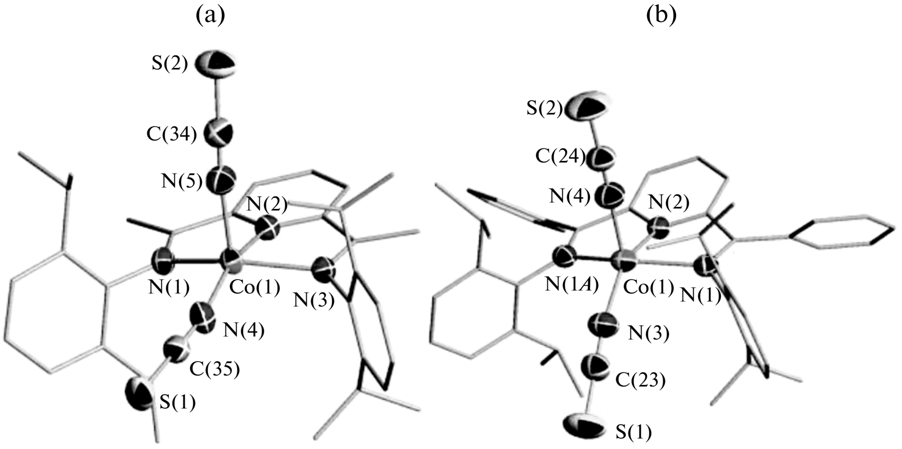

Fig. 9. Structures of complexes of the **VIII** type with R = (a) CH_3 and (b) Ph [82].

The latter substantially affects the spin-orbital interaction parameter of the Co^{2+} ion and increases the energy barrier of the SMM: $U_{eff} = 24$ K compared to $U_{eff} = 16$ K for the complex with R = CH_3. One more interesting application of the mononuclear Co^{2+} complexes for the preparation of molecular magnets was mentioned in [83]. For the preparation of the SMM with high values of U_{eff}, the effect of quantum magnetization tunneling should be reduced to minimum together with significant values of the total spin of the system S and parameter $|D|$. One of the solutions of this problem is the synthesis of mixed heterospin systems including magnetically anisotropic 3*d* metal ions and paramagnetic organic radicals [84–87].

In [83] this approach was accomplished for the complexes $Co(X)_2(D1Py)_4$ (**IX**), where X = Cl^-, NCS^-, and NCO^-; D1Py is phenylpyridyldiazomethane, whose photolysis results in the formation of triplet organic radicals that enter the ferromagnetic exchange with the Co^{3+} ion at the total spin of the system $S = 9/2$ (Fig. 10). All complexes manifest the SMM properties, but the effect of quantum magnetization tunneling decreases in the series X = NCS^-, Cl^-, NCO^- with the corresponding increase in U_{eff}. This important result unambiguously indicates the possibility of directed tuning of the magnetic properties of this type of the SMM and is explained by the authors as a change in the magnetic anisotropy parameter of the Co^{2+} ion at the variation of the nature of out-of-sphere ligands X.

It was mentioned [88] that 5*f* metals can be even more interesting with respect to the control of the quantum tunneling effect compared to lanthanides. The reason is that the 5*f* electrons occupy orbitals of a larger radius compared to the 4*f* electrons of lanthanides, which results in an increase in the spin-orbital interaction and in the corresponding increase in the magnetic anisotropy [89–92]. The authors [88] showed for the complex $[U(Tp^{Me2})_2(Bipy)]$ (**X**), where Tp^{Me2} is hydrotris(3,5-dimethylpyrazolyl)borate (Fig. 11), that the change in the structure of the complex (addition of 2,2'-bipyridine) results in the appearance of the SMM properties compared to similar derivatives containing no additional ligand molecules. As in the systems described above, the presented results are good evidence for the possibility of controlling the internal magnetic anisotropy of 4*f* and even 5*f* elements by the directed variation of the structure of the complexes.

The problems of controlling magnetization retention in the SMM in the absence of an external field, especially related to the quantum tunneling effects, are important for the practical use of these effects, for example, when using molecule magnets as elementary quantum memory cells (qubits) [5, 93]. To prepare similar devices, it is necessary to use the quantum tunneling effect for controlling the SMM properties [94].

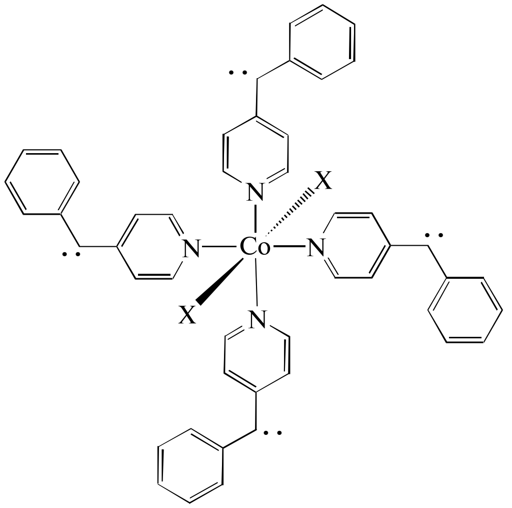

Fig. 10. Structure of heterospin complex **IX** [83].

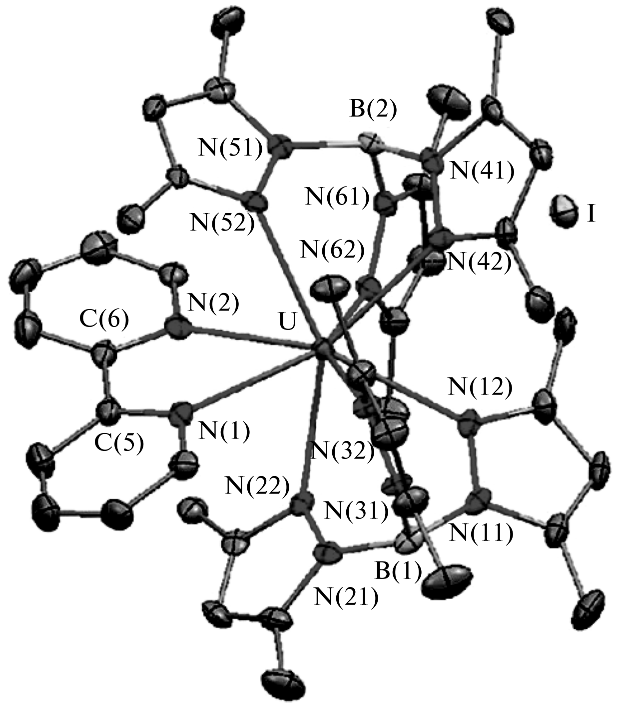

Fig. 11. Molecular structure of complex **X** [88].

This approach was accomplished by the synthesis of the supramolecular structure when using the polynuclear complexes with the SMM properties as building blocks. Supramolecular complex **XI** was synthesized by the reaction of dioxime 3-phenyl-1,5-bis(pyridinyl-2)pentane-1,5-dione and trinuclear complex $[Mn^{III}O(CH_3COO)(Py)_3](ClO_4)$ (Fig. 12).

The weak interaction between the $[Mn]_3$ fragments in the dodecanuclear architecture results in the "exchange additional magnetization" effect of quantum tunneling, which, in authors' opinion [94], is an important step for the development of multiqubit systems of information storage memory based on molecular magnets. A similar phenomenon of "exchange additional magnetization" was observed [95] together with the synthesis of heteropolynuclear clusters $[Mn_2Ni_3X_2L_4(LH)_2(|H_2O)_2]$ (X = Cl, Br; H_2L is 2-{3-(2-hydroxyphenyl)-1-*H*-pyrazol-1-yl}ethanol). In the framework of the linear chain Mn^{III}–Ni^{II}–Ni^{II}–Ni^{II}–Mn^{III}, in the case of X = Cl and Br, the paramagnetic centers are bound by a fairly strong ferromagnetic exchange interaction resulting in the total spin of the ground state $S = 7$ and pronounced magnetic anisotropy. Due to this, the heteropolynuclear complexes manifest the SMM properties, but the quantum tunneling effects differ for X = Cl and Br. The authors of the cited work explain this phenomenon important for controlling the SMM properties as a result of very weak antiferromagnetic (X = Cl) or ferromagnetic (X = Br) exchange interactions between the heteropolynuclear molecules of the complexes. The significance of the magnetic exchange for controlling the SMM properties is also urgent for the rare-earth metal complexes in which rather pronounced exchange effects is very problematic because of specific features of their electronic structures. The appearance of the residual magnetization in the polynuclear rare-earth metal complexes is a consequence of the local magnetic anisotropy [96] rather than the total significant spin of the complex molecule [41]. The hyperfine and dipole interactions result in effects of fast quantum magnetization tunneling and, therefore, in the works cited below the authors tried to align these effects by the enhancement of the magnetic exchange effect [97–100]. The asymmetrical binuclear complex manifesting the SMM properties with the composition $[Dy_2OVph_2Cl_2(Me(OH)_3] \cdot MeCN$ (H_2OVph is pyridine-2-carboxylic acid [(2-hydroxy-3-methoxyphenylmethylene)hydrazide, **XII**) in which two Dy^{3+} ions are bound by the ferromagnetic exchange interaction ($J = +5.88$ cm^{-1}, $zJ' = -1.84$ cm^{-1}) (Fig. 13) was described [100].

According to the X-ray diffraction data, the intermolecular distance Dy^{3+}–Dy^{3+} is 7.5071(5) Å, which favors the intradimer exchange of the Ising type [100]. The latter almost completely "switches off" the quantum tunneling effects and, as a consequence, substantially increases the time of magnetization relaxation. The authors [100] mention the obtained results as an important stage in the way of the development of the general theory of controlling the properties of the SMM based on rare-earth metals by fine tuning of the local structure of lanthanides.

Immobilization of SMM on technological surfaces. According to the opinion of many researchers, the immobilization of ordered SMM layers on technological surfaces would allow one to obtain devices for information recording with a density of 100 terabit per square inch, which is evidently beyond the framework of possibilities of modern devices [5, 12, 101–103]. An idea of obtaining ready SMM-based structure materials appeared immediately after the discovery of their first representatives. However, it was established soon that the predominant majority of such compounds loses these unique properties upon localization on the surface, first of all, due to the high structural instability [104, 105]. It has recently been found that the partial retention of the SMM properties is possible when these objects are localized on functionalized surfaces with sulfur-containing fragments [106–110]. However, in the case of the Mn complexes containing the $Mn_{12}Ac$ or Mn_6 clusters having the highest blocking temperatures, the situation is opposite [20, 111, 112], according to the opinion of many researchers, because of a change in the oxidation state of Mn^{3+} ions. In this case, relative success was achieved only by using the electron–ion sputtering method [112, 113]. The deposition of rare-earth metal compounds with the SMM properties on the graphite, gold, or copper surface

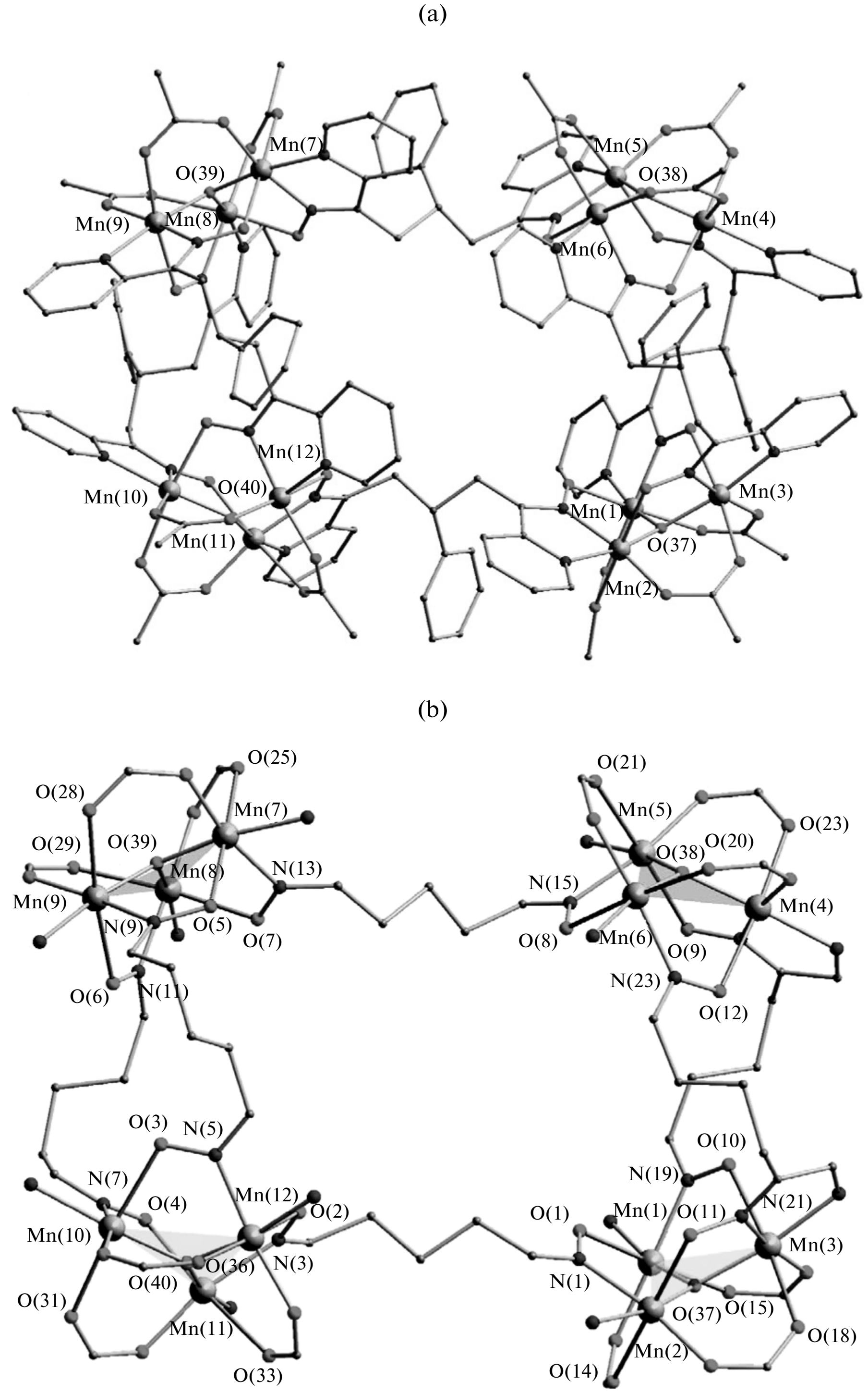

Fig. 12. Structure of complex **XI**: (a) the general structure of the complex ion and (b) the structure of the complex core reflecting bonds between individual Mn_3 clusters [94].

[114–118] is less problematic, although the general solution of this problem is yet far from detailed solution.

The development of approaches to the solution of the problem is exemplified by the results of the work [119], where the $[Mn_{12}O_{12}(Bet)_{16}(EtOH)_4]^{14+}$ cation (Bet is glycine-betaine) of complex $[Mn_{12}O_{12}(Bet)_{16}(EtOH)_4](PF_6)_{14} \cdot 4CH_3CN \cdot H_2O$ (Mn12Bet, **XIII**) (Fig. 14) is “electrostatically grafted” on the metallic gold surface functionalized by

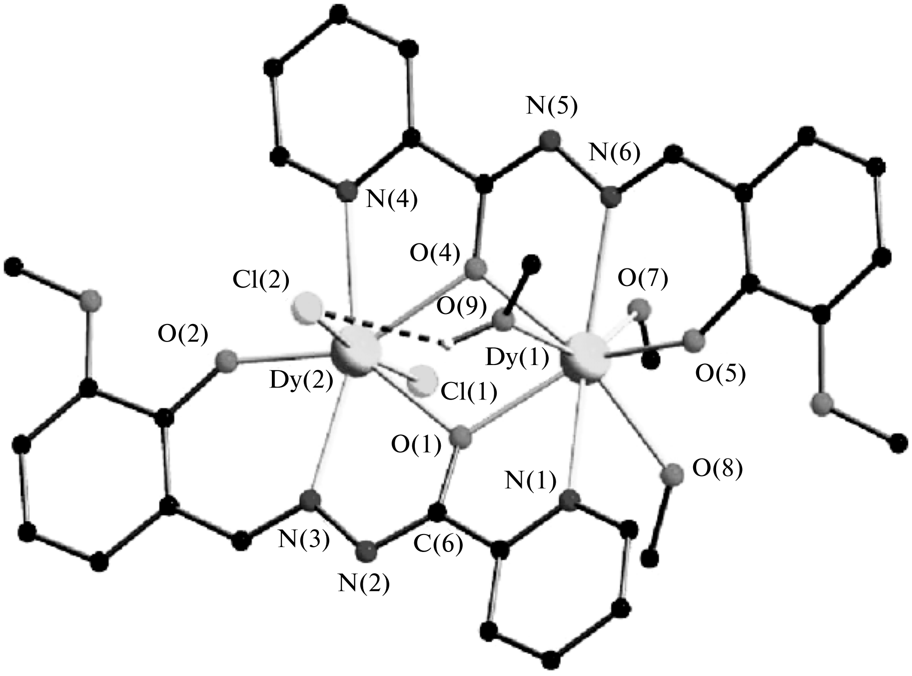

Fig. 13. Structure of complex **XII** [100].

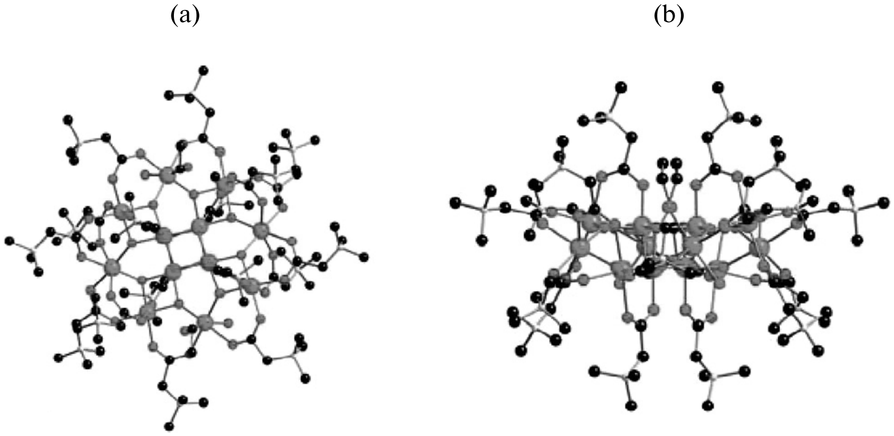

Fig. 14. Structures of complex **XIII** arranged (a) in parallel and (b) perpendicularly to the principal symmetry axis [119].

mercaptoethanesulfonate ion ($HS(CH_2)_2SO_3^-$ (MES)) or mercaptopropionic acid ($HSCH_2CH_2COOH$ (MPA)) sodium salt. Complex $Mn_{12}Bet$ was proved to exist on this surface (Fig. 15) using methods of scanning tunneling microscopy and X-ray photoemission.

The results of studies show that the $Mn^{3+/4+}$ ions of the $Mn_{12}Bet$ core are completely reduced on the MES-functionalized surface and the complex entirely loses the SMM properties. At the same time, the reduction is partial on the surface containing MPA, and some manganese ions retain the initial oxidation states. The latter serves as a reason for the retention of the properties of molecular magnets in the adsorbed molecules of the complex, which seems [119] to be very promising for further studies.

Interesting results concerning the retention and controlling the properties of the SMM supported on the metallic surface are given in [120], where the heteronuclear complex $[Fe_3Cr(L)_2(Dpm)_6]$ (**XIV**) (H_3L is 11-(acetylthio)-2,2-bis(hydroxymethyl)undecan-1-ol, Hdpm is dipivaloylmethane) was synthesized (Fig. 16).

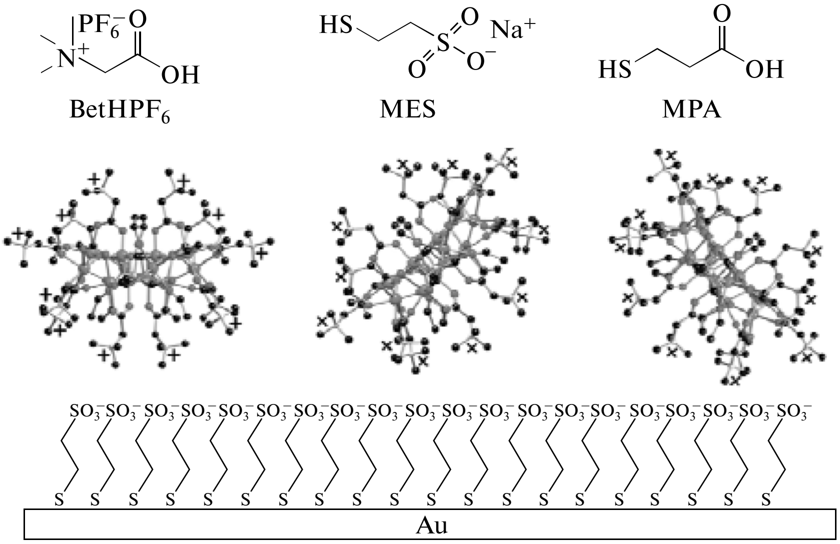

Fig. 15. Scheme of the adsorption of complex **XIII** on the functionalized metallic gold surface [119].

It was shown by magnetic measurements and X-ray circular dichroism that complex **XIV** immobilized on the metallic gold surface almost completely retained the magnetic properties of the initial product, which was prepared as a heteronuclear analog of the complex containing the Fe_4 core with the same ligands [106, 107, 121]. The ferrimagnetic exchange in the homopolynuclear and heteropolynuclear complexes (**XIV**) was found to result, as a whole, in a fairly high spin of the ground state ($S = 5$ and 6, respectively), and the exchange parameters of the heteronuclear derivative are $J_{\mathrm{Fe-Cr}} = 16.34$ cm^{-1}, $J_{\mathrm{Fe-Fe}} = 0.57$ cm^{-1}, which in combination with a significant magnetic anisotropy of the ions is a reason for the appearance of the SMM properties that remain nearly unchanged in the state adsorbed on the metallic gold surface. The presented results unambiguously prove the possibility of increasing the total spin of the ground state, one of the necessary conditions for the manifestation of the SMM properties, by the chemical variation of details of the fine structure of molecule magnets with the retention of these features when similar systems are immobilized on technological surfaces.

Positive results of supporting coordination rare-earth metal compounds with the SMM properties were also obtained with respect to the so-called "double-decker" phthalocyanine complexes [122–125], and some their representatives can form self-assembled domain structures on the surface of pyrolytic graphite [126]. The 2D supramolecular self-organization of the terbium(III) complexes with phthalocyanine ligands (**XV**) (Fig. 17) was described [116]. It was shown that when immobilizing on the pyrolytic graphite surface these complexes immediately form nanocrystals containing up to 6000 individual molecules of the complexes, and the thickness of these nanocrystals corresponds to the monomolecular layer (Fig. 18).

A similar character of self-organization turned out to be very interesting from the viewpoint of the SMM properties of complex **XV**. It was shown [116] that the magnetic properties of the adsorbed nanocrystals almost did not differ from the properties of the individual compound. This was confirmed by the experimental data obtained for individual compound **XV** with a SQUID magnetometer (Fig. 19a) and for the adsorbed nanocrystals using the magnetic circular dichroism method (Fig. 19b). These data show that both systems at 7 K have a pronounced magnetization hysteresis, and the character of the magnetic proper-

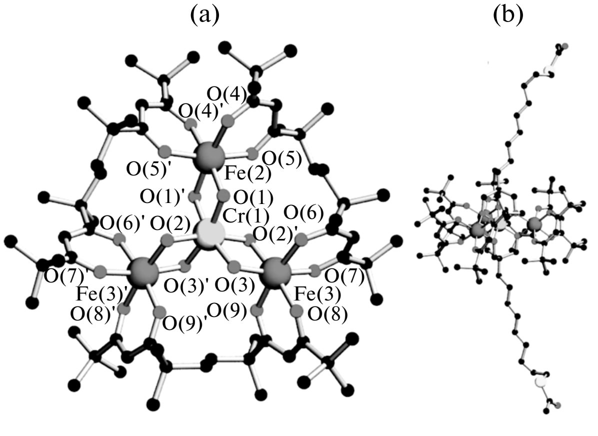

Fig. 16. Structure of complex **XIV**: structures of (a) the cluster core and (b) the whole complex [120].

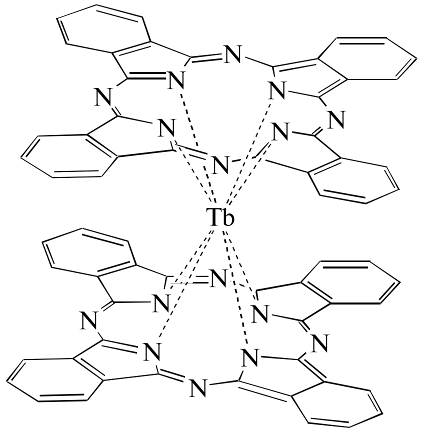

Fig. 17. Molecular structure of the terbium(III) complex of the **XV** type [116].

ties of the complex remains almost unchanged upon adsorption.

The latter fact will allow the further use of graphite supports for the formation of supramolecular architectures of molecule magnets, which should assume, in principle, “fine tuning” of their physical, first of all, magnetic characteristics [127].

It should be mentioned in conclusion that the works cited above serve as a bright confirmation of the fact that molecular magnetism is presently a dynamic and highly demanded area of research. In the early 1990s the main problem was the synthesis of molecule magnets with an increased blocking temperature, whereas nowadays the design and practical preparation of polyfunctional materials with the SMM properties are urgent. Chemical science, first of all, coordination chemistry, plays a special role in these studies, because these scientific disciplines make it possible to prepare molecule magnets with specific characteristics corresponding to various technological tasks. Evidently, when solving possible problems, the major aim will be the representation of these objects as thin films integrated into a certain device and capable of giving a certain response to both the applied external magnetic field and electromagnetic radiation, a change in the external pressure, electrical fields, etc. rather than the preparation of polyfunctional crystalline materials. In addition to coordination chemistry, similar studies require to use statements of organic and especially organometallic chemistry, surface chemistry, and solid state chemistry. As follows from the works cited above, the last break-through achievements that join the indicated chemical disciplines are the successful immobilization of molecule magnets on the surface with the retention and possibility of variation of their technological properties and especially the synthesis of the SMM based on 4*f* elements. In the last case, the theoretical understanding of similar objects, especially the establishment of important “structure–property” correlations on the basis of quantum-chemical calculations [128, 129] are especially significant, and the main attention will be given in future to the establishment of a relationship between the chemical environment of the metal center and magnetic anisotropy parameters [130–132]. As a whole, it can be mentioned that the possibilities and directions of future studies of molecule magnets are infinite: from the preparation of magnetic materials substantially smaller than those of traditional sizes (one molecule, polymer chain, monomolecular coating) to the production of the corresponding technological devices that make it possible to perform directed manipula-

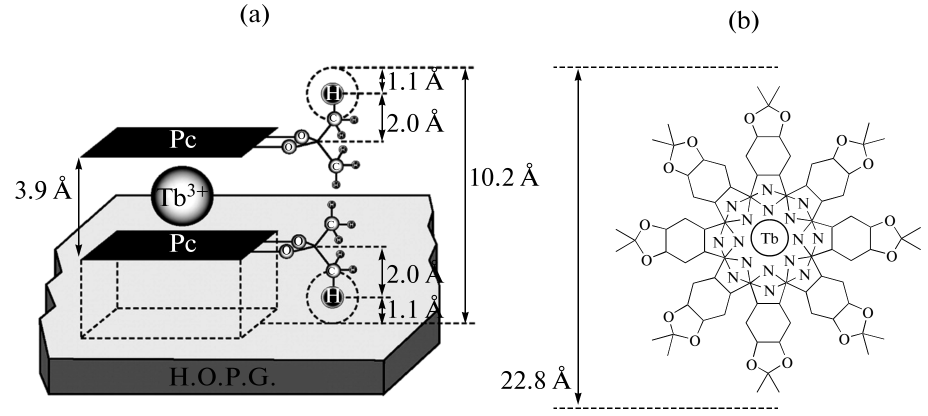

Fig. 18. (a) Scheme of the adsorbed state of complex **XV** and (b) its horizontal projection [116].

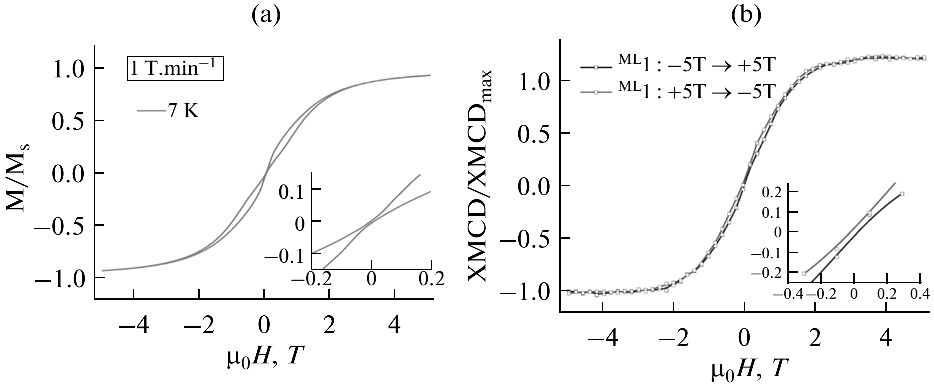

Fig. 19. (a) Magnetization hysteresis of the single-crystal sample of complex **XV** (the amplified region of weak magnetic fields is shown in inset) and (b) the monolayer of the adsorbed complex (the amplified central part of hysteresis is shown in inset) at 7 K [116].

tions with spins of individual molecules in the picosecond range.

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