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Photochromic single-molecule magnets based on oxocarboxylate Mn_{12} clusters and mononitrosyl Ru complexes

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Mono- and dianionic oxocarboxylate Ru—Mn_{12} clusters, $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]_2$ (R = Ph (**1**)), $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = C_6F_5 (**2**), CH_2Cl (**3**), R = $CHCl_2$ (**4**)), and $[RuNO(NH_3)_4OH][Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = CH_2Cl (**5**), $CHCl_2$ (**6**)) containing photochromic mononitrosyl ruthenium complexes as cations were synthesized. The magnetic properties of the complexes in static and alternating magnetic fields were studied, and compounds **1**—**6** were found to be molecular nanomagnets. By IR spectroscopy, they were shown to exhibit also photochromic properties.

Key words: synthesis, bifunctional compounds, oxocarboxylate Mn_{12} clusters, single-molecule magnets, photochromism, mononitrosyl Ru complexes, magnetic hysteresis, magnetic susceptibility.

In the last two decades, a new line of research has been advanced in the field of molecular magnets related to the synthesis and studies of molecular nanomagnets (zero-dimension magnets, single-molecule magnets, SMM).[1] Molecular nanomagnets are polynuclear high-spin clusters the structure of which is composed of magnetic nuclei of transition and/or rare earth metal ions surrounded by a shell of organic ligands. The shell protects the magnetic nucleus from intermolecular magnetic interactions. These molecular materials possess unique magnetic properties (superparamagnetism, slow magnetic relaxation, blocking and quantum tunneling of magnetization, quantum interference, magnetic bistability, and so on), which are related to the magnetism of a single molecule.[2] Unusual magnetic properties of nano-sized magnets arise through combination of the high spin value of the ground spin state and negative magnetic anisotropy. Research into compounds with these unique magnetic characteristics is of considerable interest not only for the fundamental science but also for various practical applications.[3]

An important advantage of single-molecule magnets compared with other magnetic nanoparticles is that they are identical and their structure and magnetic properties can be deliberately adjusted by selecting molecular building blocks and conditions of chemical assembly. This way of preparing larger nanomolecules from small blocks is more efficient than the traditional ultraminiaturization (top-down) of the classical bulk magnets.[4] This also allows preparation of polyfunctional compounds containing other functional blocks, for example, optical or conducting ones, based on single-molecule magnets. The molecular materials whose magnetic properties can reversibly change under an external action are of high scientific and practical interest. For example, recently,[5] radical ion salts containing cationic single-molecule magnets, $[Mn_4(hmp)_6(MeCN)_2]^{4+}$ and $[Mn_2(5\text{-MeOSaltmen})_2(MeCN)_2]^{2+}$, and conductive anionic subsystems, $[Pt(mnt)_2]^{n-}$ and $[Ni(dmit)_2]^{n-}$, were synthesized (hmp is 2-hydroxymethylpyridine, 5-MeO-Saltmen is *N*,*N*´-(1,1,2,2-tetramethylethylene)-bis(5-methoxysalicylidene) iminate, mnt is 1,2-dicyano-1,2-ethylenedithiolate, dmit is 1,3-dithiol-2-thione-4,5-dithiolate). These salts are conducting, and at helium temperatures, they exhibit magnetic properties typical of molecular nanomagnets. However, the conducting and magnetic blocks in these systems behave independently, because the salts are insulators at low temperatures. A photochromic single-molecule magnet based on Mn_{12} clusters with the azobenzene ligand is known.[6] It was shown that the cluster containing the *cis*-isomer of the ligand has a higher magnetization and slower magnetization relaxation than the cluster with *trans*-azobenzene as the ligand. A photoluminescent single-molecule Mn_4 magnet with 9-anthracenecarboxylic acid as the ligand was obtained.[7]

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We studied the synthesis of photochromic single-molecule magnets based on anionic oxocarboxylate Mn_{12} clusters with cationic mononitrosyl ruthenium complexes as counter-ions. The six-coordinate cationic ruthenium complexes ($[RuNOL_4X]^{2+}$, L = en, NH_3; X = Cl, OH) attract considerable attention, as they exhibit photochromic properties: exposure to light at a particular wavelength at low temperatures gives rise to two long-lived metastable states (MS1 and MS2); MS1 is generated on exposure of the complexes to blue-green light (350—580 nm), while MS2 is formed from MS1 under infrared irradiation (1064 nm). The reverse transition from the metastable states to the ground (GS) states is induced by irradiating the sample at 600—900 nm or by heating to room temperature.[8]

X-Ray diffraction studies showed that the formation of two long-lived metastable states in mononitrosyl Ru complexes is associated with isomerization of the NO group. In the ground state, the NO group is linked to the metal through nitrogen, while in MS1 it is linked through oxygen. In MS2, the metal atom coordinates both O atoms of the nitrosyl group.[9] As the magnetic components for the synthesis of bifunctional compounds, we used oxocarboxylate Mn_{12} clusters. These clusters represent the best studied family of single-molecule magnets and have one of the highest known blocking temperature of magnetization.[10] In addition, neutral clusters of this family have an important feature: they can oxidize the iodide ion to form mono-, di-, and trianionic Mn_{12} clusters, which retain the behavior of single-molecule magnets.[11] Using neutral Mn_{12} clusters with various oxocarboxylate ligands and mononitrosyl ruthenium iodide complexes, we prepared a series of mono- and dianionic Mn_{12} clusters containing mononitrosyl ruthenium complex cations: $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]_2$ (R = Ph (**1**)), $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = C_6F_5 (**2**), CH_2Cl (**3**), R = $CHCl_2$ (**4**)), and $[RuNO(NH_3)_4OH]$-$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = CH_2Cl (**5**), $CHCl_2$ (**6**)). This work is devoted to the synthesis and study of photochromic and magnetic properties of these new bifunctional compounds **1**—**6**.

Results and Discussion

The oxidation of complex ruthenium iodides $[RuNO(en)_2Cl]^{2+}$ or $[RuNO(NH_3)_4OH]^{2+}$ with neutral $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ clusters (R = Ph, CH_2Cl, $CHCl_2$, C_6F_5) was carried out in MeCN at room temperature (see, for example, Scheme 1).

Scheme 1

$$[RuNO(en)_2Cl]I_2 + [Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4] \longrightarrow$$

$$\longrightarrow [RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4] + I_2$$

2

Since the initial complex ruthenium iodide is poorly soluble in MeCN, the reaction mixture was stirred for a long period of time (6—7 h). The reaction was accompanied by evolution of molecular iodine, which was extracted into hexane. The process was stopped when a fresh portion of hexane added to the reaction solution remained colorless. Then the solvent was removed, the dry residue was dissolved in CH_2Cl_2, the solution was filtered, and hexane was carefully added to the solution. After 24 h, the precipitated brown powder was filtered off, washed with hexane, and dried *in vacuo*. Numerous attempts to obtain single crystals by slow diffusion were not a success. The composition of the obtained compounds was established from the data of elemental analysis, IR spectroscopy, and electrospray ionization mass spectrometry.

The IR spectra of the reaction products exhibited, along with the bands typical of Mn_{12} clusters, also a new band at 1882—1910 cm^{-1} corresponding to the NO stretching vibrations of the cation (Fig. 1). Electrospray ionization mass-spectrometric studies of solutions of the isolated complexes in MeCN showed the presence of signals both in the negative- and positive-ion modes of the spectra associated with the anion and the cation, respectively. Thus the negative-ion ESI mass spectrum of **2** contains peaks at *m/z* 2113.47 and 1408.98 corresponding to the $[Mn_{12}O_{12}(O_2CC_6F_5)_{16}]^{2-}$ (**2´**) and $[Mn_{12}O_{12}(O_2CC_6F_5)_{16}]^{3-}$ (**2″**) molecular ions, respectively (Fig. 2, *a*). Ion **2´** is formed upon the loss of four water molecules by the starting dianionic cluster and **2″** results from reduction of **2´** *in situ*. The ESI mass spectrometer functions as an electrochemical cell, the dianionic cluster is reduced under the experimental conditions, and the $[Mn_{12}O_{12}(O_2CC_6F_5)_{16}]^{3-}$ anion is found in the negative-ion mode. The isotope distribution of these ions (insets in Fig. 2, *a*) exactly corresponds to the theoretical isotope distribution. The absence, in the mass spectrum of **2**, of the singly charged molecular ion, $[Mn_{12}O_{12}(O_2CR)_{16}]^-$, observed usually in the negative-ion ESI mass spectra of

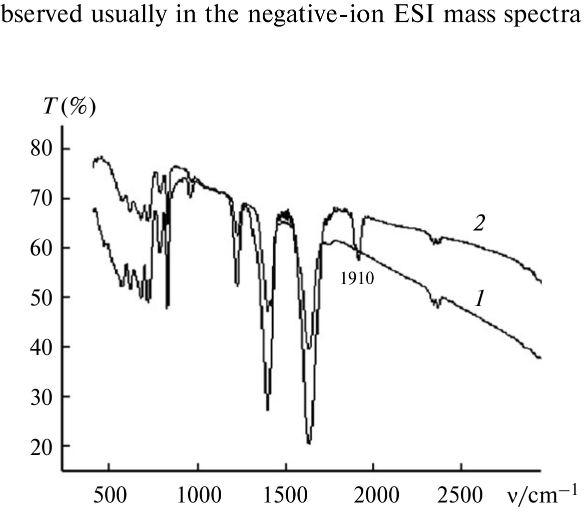

Fig. 1. IR spectra of the initial cluster $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (*1*) and compound **6** (*2*).

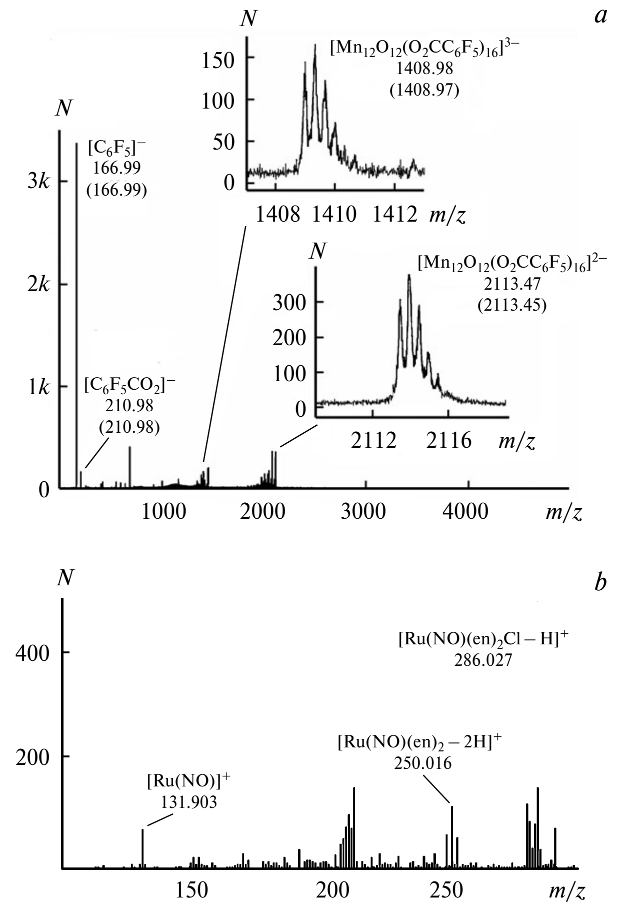

Fig. 2. Electrospray ionization mass spectra of compound **2** in a MeCN solution: negative (*a*) and positive (*b*) ion modes; the experimental and calculated (in parentheses) *m/z* values are indicated.

neutral $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ clusters,[12] attests to the reduction of the cluster to the dianion during the reaction with $[RuNO(en)_2Cl]I_2$. The fragments of $[RuNO(en)_2Cl]^{2+}$ were found in the positive-ion mass spectrum of **2** (Fig. 2, *b*); these are formed upon destruction of the cation during ionization.

The photochromic properties of the obtained compounds were studied by IR spectroscopy. Infrared spectroscopy is traditionally used to identify and estimate the populations of metastable states (MS1 and MS2) in mononitrosyl transition metal complexes.[13] Note in particular that compounds **1—6**, unlike the starting mononitrosyl Ru complexes, were dark brown-colored, and this circumstance substantially complicated the investigation of samples **1—6** upon irradiation. Therefore, the preliminary manufacture of homogeneous transparent KBr discs with the samples was very important and critical. The generation of MS1 is known to be very sensitive to the wavelength (325—550 nm); therefore, to choose the optimal wavelength, the samples were first irradiated for 30 min at various wavelengths (λ = 325, 442, 458, 476, 488, and 514 nm). As a results, the optimal wavelength giving rise to the highest population of MS1 was determined. Then the dependence of the population of the metastable state on the light exposure was studied for these samples at the optimal wavelength (Table 1).

The irradiation was carried out up to the saturation of the spectrum, *i.e.*, until the spectrum ceased to change on further irradiation. Depending on the nature of the sample, irradiation time reached in some cases 3.5 h. Generation of the first metastable state (MS1) in which the NO group is bound to Ru through the O atom was detected based on the decrease in the intensity of the NO stretching band and appearance of a new band shifted by ~135 cm^{-1} to lower frequency with respect to the NO band in the ground state. The difference IR spectrum of complex **2** obtained by subtraction of the spectrum before irradiation from the spectrum after irradiation at λ = 442 nm is shown in Fig. 3. After exposure to light, all spectra of compounds **1—6** exhibited a new band shifted to low frequencies, which was indicative of generation of the first metastable state in compounds **1—6**. The second metastable state MS2 of **2** with both nitrosyl O atoms coordinated to Ru was generated by successive irradiation at 442 and 1064 nm. During the process, the intensity of the band of the first metastable state decreased and a new NO stretching band associated with the formation of the second metastable state (MS2) appeared at 1550 cm^{-1}. To verify whether the process was fully reversible, after generation of the metastable state, the samples were exposed to red light (λ = 660 nm), which is known to transform the metastable states of mononitrosyl Ru complexes to the ground state. For all of the samples **1—6**, the NO vibration band of the ground state was fully restored. This indicated that no NO evolution took place on irradiation, all spectral changes being related to the formation of metastable states (structural isomers). Analysis of the obtained results showed that the photochromic properties of the synthesized anionic clusters with cationic mononitrosyl Ru complexes as counterions depend on the nature of the photochromic cation. Thus the clusters with the $[RuNO(en)_2Cl]^{2+}$ cation possess a much higher population of the metastable state MS1 than the clusters containing the $[RuNO(NH_3)_4OH]^{2+}$ cation.

Table 1. Population of the metastable state (*P*(MSI)) in compound **2** as a function of light exposure (*Q*)

λ/nm	*Q* /J cm^{-2}	*P*(MSI) (%)	ν(NO) /cm^{-1}	*T*/K
—	—	—	1891/1876	300
—	—	—	1892/1875	80
442	113	8	1756/1737	80
442	226	16	1756/1737	80
442	452	26	1756/1737	80
442	565	26	1756/1737	80

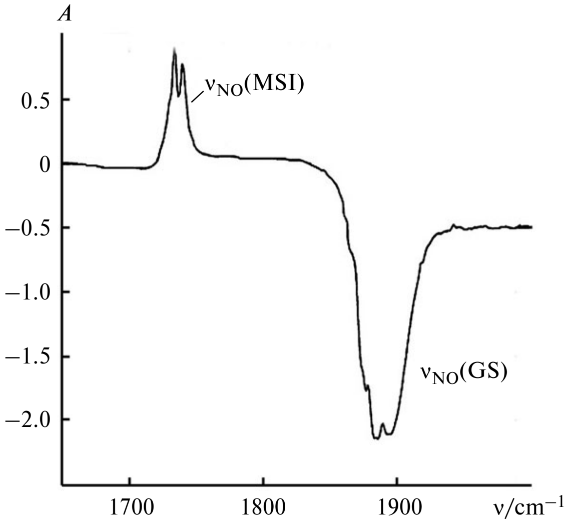

Fig. 3. Difference IR spectrum of cluster **2** obtained by subtraction of the spectrum before irradiation from the spectrum after irradiation at $\lambda = 442$ nm.

The magnetic properties of compounds **1—6** were studied by SQUID magnetometry. The temperature dependences of the static magnetic susceptibility were measured on polycrystalline samples **1—6** at temperatures of 2—300 K in a 0.1 T magnetic field. As the temperature is decreased to ~150 K, the $\chi_M T$ values for all compounds gradually decrease (Fig. 4.) Further decrease in the temperature induces a fast growth of $\chi_M T$ values, which reach a maximum at 7—15 K and then sharply drop. This behavior of $\chi_M T$ as a function of temperature is typical of the family of Mn_{12} complexes.**[10,11]** The $\chi_M E$ values in the maximum for complexes **2—5** are 40—50 cm^3 K mol^{-1}, which is typical of mono- and dianionic oxocarboxylate Mn_{12} clusters, whereas for complex **1** this value is twice higher (100 cm^3 K mol^{-1}); this confirms the composition of the complex (the ratio of the cluster monoanion to the doubly charged cation is 2 : 1). The field dependences of the magnetization of anionic clusters were studied; they demonstrated hysteresis loops at low temperatures (Fig. 5).

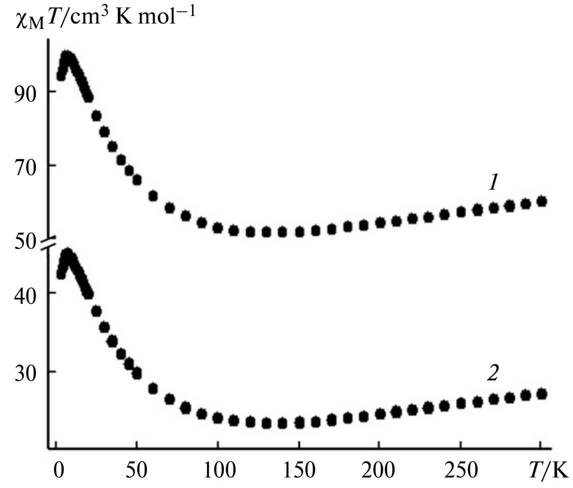

Fig. 4. Dependence of $\chi_M T$ on the temperature for polycrystalline samples of **1** (*1*) and **6** (*2*), χ_M is the static molar magnetic susceptibility measured at 1 kG.

The magnetic susceptibility was also studied in alternating magnetic field at different frequencies (ν) in the region of 1.0—1500 Hz. The products of the real part of the dynamic magnetic susceptibility by the temperature in the saturation region are in good agreement with the values determined by measurements of the static magnetic susceptibility. Compounds **1—6** showed a regular shift of the peak of the $\chi''(E)$ curve with increase in frequency, which is typical of high-spin clusters (Fig. 6). The maximum of χ'' arises at a temperature at which the spin relaxation frequency coincides with the external magnetic field frequency ν. The thermal relaxation time of magnetization (τ) obeys the Arrhenius law: $\tau = \tau_0 \exp(U_{eff}/kT)$, where $\tau = 1/2\pi\nu$, k is the Boltzmann constant. Using the temperature dependences of the χ'' maxima at different frequencies, the effective energy barriers to magnetization relaxation U_{eff} were determined for compounds **1** and **6** to be similar (59 and 58 K, respectively) (Fig. 7). In the case of compound **6**, this result was quite unexpected, as for known dianionic Mn_{12} clusters, the barrier is usually ~30 K. It is known that the local environment of Mn_{12} clusters affects the magnetic relaxation dynamics.**[12,14]** In compound **6**, hydrogen bonds may form between the NH_3 and OH ligands of the cation and the dichloromethyl groups of the carboxylate ligands of the cluster dianion, and this may affect the magnetization relaxation process, resulting in a higher barrier (U_{eff}).

Thus, we synthesized mono- and dianionic clusters, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ with mononitrosyl Ru complexes as cations. The photochromic properties of the clusters were studied by IR spectroscopy. Irradiation of the

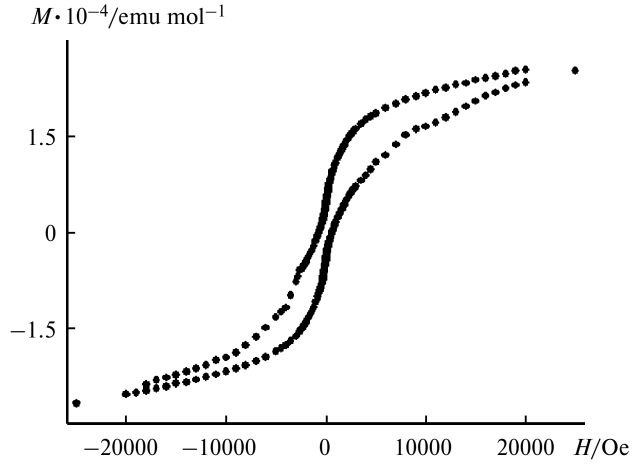

Fig. 5. Magnetic hysteresis loop for compound **6** at 2 K.

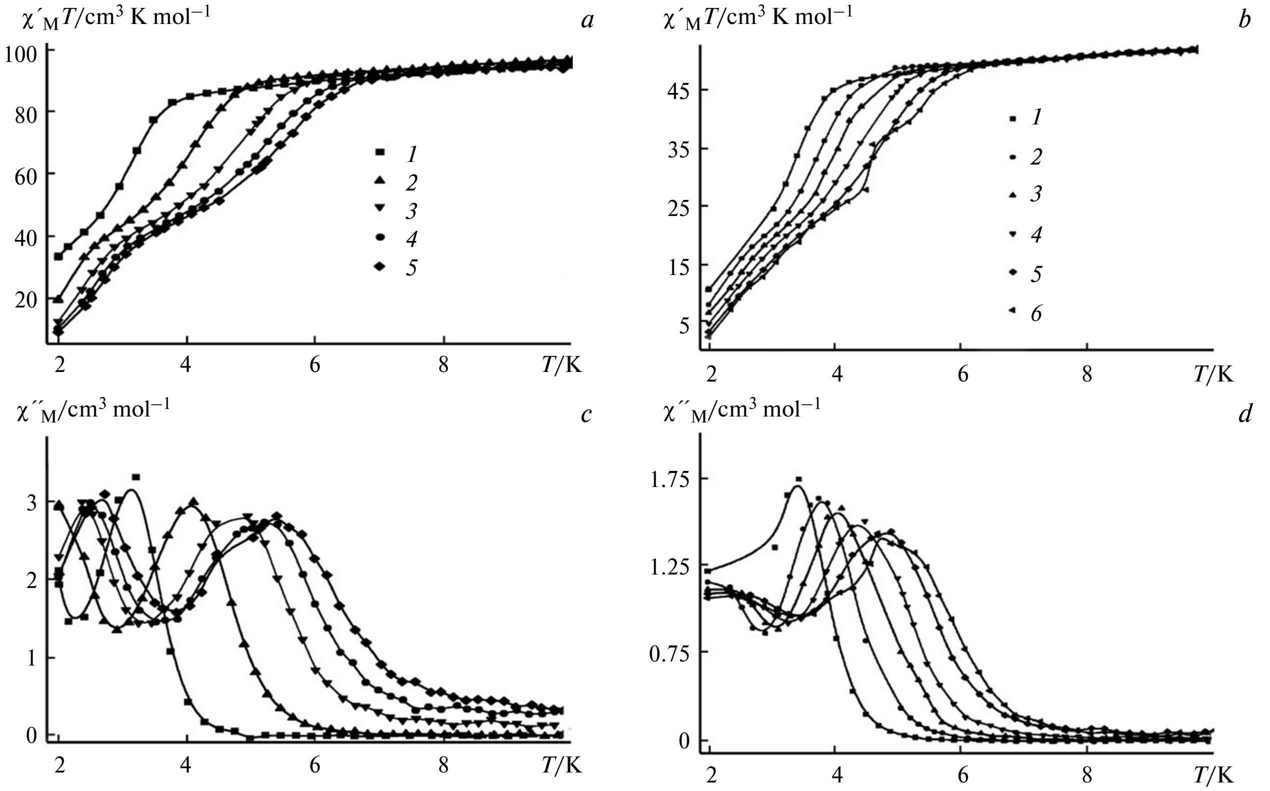

Fig. 6. Temperature dependences of the real (*a*, *b*) and imaginary (*c*, *d*) parts of magnetic susceptibility measured for compounds **1** (*a*, *c*) and **6** (*b*, *d*) in alternating magnetic field at invariable frequencies: 1 (*1*), 4 (*2*), 40 (*3*), 300 (*4*), 1400 (*5*) Hz (*a*, *c*); 10 (*1*), 40 (*2*), 100 (*3*), 300 (*4*), 800 (*5*), and 1500 Hz (*6*) (*b*, *d*).

clusters in the blue-green spectral region at 80 K gives rise to a new NO stretching band in the IR spectrum shifted by 135 cm^{-1} to lower frequency with respect to the position of this band before irradiation (1870—1910 cm^{-1}), indicating the formation of a metastable state (MS1). The populations of the metastable state were estimated from the ratio of the areas of the NO vibration band in the ground state before and after irradiation. The highest population of MS1 (26%) was found for the dianionic cluster (R = C_6F_5) containing the $[RuNO(en)_2Cl]^{2-}$ cation. The magnetic properties of the obtained compounds in static and alternating magnetic fields were studied by SQUID magnetometry, and the compounds were found to be molecular nanomagnets (SMMs). For molecular nanomagnets **1** and **6**, the heights of potential barriers (59 and 58 K, respectively) and magnetic relaxation frequencies were determined.

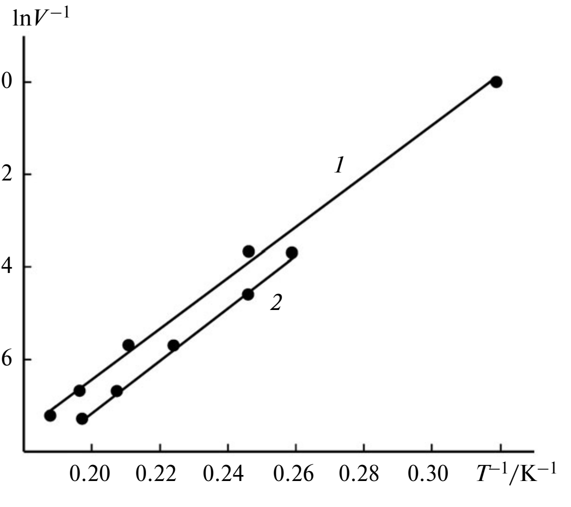

Fig. 7. Natural logarithm of the magnetization relaxation time *vs.* E^{-1} for compounds **1** (*1*) and **6** (*2*) ($\tau = 1/2\pi\nu$); $U_{\text{eff}} = 59$ K, $(\tau_0)^{-1} = 1.6 \cdot 10^8$ s^{-1} (*1*); $U_{\text{eff}} = 58$ K, $(\tau_0)^{-1} = 5.4 \cdot 10^8$ s^{-1} (*2*).

Experimental

All manipulations were carried out under aerobic conditions using Aldrich and Fluka chemicals as received. The $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ cluster was synthesized by a published procedure;[15] by ligand substitution, it was converted to the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ clusters, where R = Ph, CH_2Cl, $CHCl_2$, and C_6F_5.[10a,b,11b,16] The $[RuNO(NH_3)_4OH]I_2$ and $[RuNO(en)_2Cl]I_2$ complexes were synthesized by the reaction of a saturated aqueous solution of KI with saturated solutions of $[RuNO(NH_3)_4OH]Cl_2$ and $[RuNO(en)_2Cl]Cl_2$, respectively. The yellow powders formed were filtered off, washed with a water—ethanol mixture, EtOH, and acetone, and dried in an air stream. The yield was 75—85% for $[RuNO(NH_3)_4OH]I_2$ and 60—70% for $[RuNO(en)_2Cl]I_2$.

Elemental analysis of compounds **1—6** was performed on a Vario MICRO Cube analyzer. Mass spectra were run on a QSTAR XL LC/MS/TOF System serial tandem mass spectrometer (MDS Sciex, Canada) in the negative ion mode. Solutions of the complexes in MeCN (10^{-4} mol L^{-1}) were used as samples. The voltage on the source capillary was maintained constant (–2.5 kV). The potential difference between the inlet diaphragm and the skimmer was optimized at –15 V to minimize the fragmentation of the initial ions in this area and to avoid loss of sensitivity. Mass spectra were recorded and the results were analyzed using Analyst QS software.

The infrared spectra of complexes **1—6** were recorded on a Nicolet 5700 FTIR spectrometer. The studies were carried out for KBr pellets containing 1—2 mg of the studied sample. A pressed pellet was fastened to a copper finger by a silver paste and placed in a vacuum chamber having two potassium bromide windows and equipped with a thermocouple for temperature recording. The chamber was evacuated. The IR spectrum was recorded *in vacuo* at room temperature, and then the sample was slowly cooled by liquid nitrogen, and the IR spectrum was measured at 80 K. Then for determining the optimal wavelength, the sample was irradiated at different wavelengths (λ = 325, 442, 458, 476, 488, 514 nm) for 30 min and the spectra were recorded. For generation of MS1, a diode laser with λ = 442 nm and an intensity of 180 mW cm^{-2} was used as the light source. The irradiation time was 3 h. MS1 was converted to MS2 by irradiation with light of a Nd-YAG laser (λ = 1064 nm) with an intensity of 120 mW cm^{-2}. The irradiation time was 30 min. The complete reversibility of the process was checked by irradiating the samples after generation of the metastable state with red light (λ = 660 nm).

The magnetic properties of powdered samples **1—6** were studied by a MPMS 5XL SQUID magnetometer (Quantum Design). The dependence of the magnetic moment on the temperature $M(T)$ was measured in the temperature range of 2—300 K in a static magnetic field with strength H = 1 kOe. The dependence of the magnetic moment on the magnetic field strength $M(H)$ was determined in the range H = 0—50 kOe at 2 K. For measurements in the alternating magnetic field, the field frequency varied in the 1—1500 Hz and the amplitude was 4 Oe.

The complex $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]_2$ (1). The complex $[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]$ (0.1483 g, $5 \cdot 10^{-2}$ mmol) was dissolved in 70 mL of a MeCN—CH_2Cl_2 solvent mixture (3 : 4). Dry $[RuNO(en)_2Cl]I_2$ (0.014 g, $2.5 \cdot 10^{-2}$ mmol) was added to the resulting solution and the mixture was stirred for 6 h. The reaction was accompanied by evolution of molecular iodine, which was removed by extraction with hexane. The extraction was stopped when the fresh portion of hexane added to the reaction solution remained colorless. Then the solution was filtered and the solvents were evaporated. The dry residue was dissolved in CH_2Cl_2 (20 mL), and hexane (100 mL) was carefully added. The flask containing the reaction mixture was placed in a refrigerator. After 24 h, a powdered precipitate formed. This was filtered off, washed with hexane and diethyl ether, and dried *in vacuo*. Yield 0.0589 g (72%). Found (%): C, 45.34; H, 4.03; N, 1.52. $C_{228}H_{192}ClMn_{24}N_5O_{97}Ru$. Calculated (%): C, 45.55; H, 3.20; N, 1.17. IR, ν/cm^{-1}: 1597, 1537, 1524, 1406, 1176.8, 1069, 1025, 717, 676 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = 1882 cm^{-1}.

The complex $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4]$ (2). The complex $[Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4]$ (0.2966 g, $6.46 \cdot 10^{-2}$ mmol) was dissolved in 20 mL of MeCN. Dry $[RuNO(en)_2Cl]I_2$ (0.034 g, $6.46 \cdot 10^{-2}$ mmol) was added to the resulting solution, and the mixture was stirred for 6 h. The reaction was accompanied by evolution of molecular iodine, which was removed by extraction with hexane. The extraction was stopped when the fresh portion of hexane added to the reaction solutin remained colorless. Then the solution was filtered and the solvents were evaporated. The dry residue was dissolved in CH_2Cl_2 (20 mL), and hexane (100 mL) was carefully added. The flask containing the reaction mixture was placed in a refrigerator. After 24 h, a powdered precipitate formed. This was filtered off, washed with hexane and diethyl ether, and dried *in vacuo*. Yield 0.1542 g (48.7%). Found (%): C, 30.45; H, 0.81; N, 1.77. $C_{116}H_{24}ClF_{80}Mn_{12}N_5O_{49}Ru$. Calculated (%): C, 30.35; H, 0.52; N, 1.53. IR, ν/cm^{-1}: 1599, 1549, 1524, 1491.7, 1391.5, 1289, 1117.8, 996, 947 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = 1892.2 cm^{-1}.

The complex $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ (3). The complex $[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ (0.0964 g, $4.0 \cdot 10^{-2}$ mmol) was dissolved in 20 mL of MeCN. Dry $[RuNO(en)_2Cl]I_2$ (0.0216 g, $4 \cdot 10^{-2}$ mmol) was added to the resulting solution, and the mixture was stirred for 6 h. Then the operations described for compound **2** were performed to give compound **3**. Yield 0.0525 g (48.7%). Found (%): C, 16. 58; H, 2.54; Cl, 22.74; N, 3.14. $C_{36}H_{56}Cl_{17}Mn_{12}N_5O_{49}Ru$. Calculated (%): C, 15.96; H, 2.07; Cl, 22.28; N, 2.58. IR, ν/cm^{-1}: 1399.3, 1250.8, 1146, 1055, 934 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = = 1885.8 cm^{-1}.

The complex $[RuNO(en)_2Cl][Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (4). The complex $[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (0.1188 g, $4.0 \cdot 10^{-2}$ mmol) was dissolved in 20 mL of MeCN. Dry $[RuNO(en)_2Cl]I_2$ (0.0216 g, $4 \cdot 10^{-2}$ mmol) was added to the resulting solution, and the mixture was stirred for 6 h. Then the operations described for compound **2** were performed to give complex **4**. Yield 0.0897 g (69%). Found (%): C, 14.20; H, 2.52; Cl, 35.98; N, 2.74. $C_{36}H_{40}Cl_{33}Mn_{12}N_5O_{49}Ru$. Calculated (%): C, 13.26; H, 1.23; Cl, 35.95; N, 2.15. IR, ν/cm^{-1}: 1597.3, 1414, 1358, 1225, 965, 822, 783 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = 1910 cm^{-1}.

The complex $[RuNO(NH_3)_4OH][Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ (5). The complex $[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ (0.0484 g, $2.0 \cdot 10^{-2}$ mmol) was dissolved in 20 mL of MeCN. Dry $[RuNO(NH_3)_4OH]I_2$ (0.0094 g, $2 \cdot 10^{-2}$ mmol) was added to the resulting solution, and the mixture was stirred for 6 h. Then the operations described for compound **2** were performed to give complex **5**. Yield 0.0309 g (59.4%). Found (%): C, 14.97; H, 2.33; Cl, 21.73; N, 2.23. $C_{32}H_{53}Cl_{16}Mn_{12}N_5O_{50}Ru$. Calculated (%): C, 14.57; H, 2.01; Cl, 21.45; N, 2.66. IR, ν/cm^{-1}: 1582, 1397, 1252, 936, 790 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = 1897 cm^{-1}.

The complex $[RuNO(NH_3)_4OH][Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (6) was synthesized in 52% yield by a procedure similar to the procedure of preparation of complex **5**. Found (%): C, 14.48; H, 2.09; Cl, 34.52; N, 1.46. $C_{38}H_{51}Cl_{32}N_5Mn_{12}O_{50}Ru$. Calculated (%): C, 13.93; H, 1.56; Cl, 34.70; N, 2.14. IR (KBr), ν/cm^{-1}: 1582, 1396, 1254, 936, 791 (cluster anion). In addition, the spectrum contained the characteristic band ν(NO) = 1900 cm^{-1}.

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