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36-Nuclear Anionic Cobalt(II) and Nickel(II) Complexes in Solid-Phase Insertion Reactions

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Abstract—The reactions of single crystals containing 36-nuclear anionic complexes of cobalt(II), $(NBu_4)_8[Co_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 2.5H_2O \cdot CH_3OH$ (**I**), and nickel(II), $(NBu_4)_8[Ni_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 6H_2O \cdot 2C_2H_5OH$ (**II**) and $(NHEt_3)_3[Ni_{36}(NHEt_3)(H_2O\text{-}\kappa O)_{12.25}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_4(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{20}(\mu_4\text{-}Me_2Mal)_6] \cdot 39H_2O$ (**III**), with solutions of 1,4-dioxane and a 0.1 M solution of Dabco (Dabco is 1,4-diazabicyclo[2.2.2]octane) in EtOH are studied. An ethanol solution of Dabco dissolves the crystals of the complexes, whereas the insertion of the solvent molecules with single crystal retention (for the cobalt compound containing tetrabutylammonium cation, **I**), cracking (for the nickel analog, **II**), or dissolution (for the cobalt complex containing triethylammonium, **III**) occurs in 1,4-dioxane. The X-ray diffraction analyses show the substitution of the uncoordinated water and ethanol molecules in the starting compound by 1,4-dioxane molecules in the structure of compound **I** to form $(NBu_4)_8[Co_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 7C_4H_8O_2$ (**IV**), which is accompanied by a change in the conformation and the shift of tetrabutylammonium cations, indicating a possibility of the modification of the 36-nuclear *d*-metal complexes with the malonic acid derivatives in the solid-phase resolvation reactions (CIF files CCDC no. 1557499 (**III**) and 1557500 (**IV**)).

Keywords: polynuclear *d*-metal complexes, dimethyl malonates, solid-phase reactions

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INTRODUCTION

The coordination compounds of *d*-metals containing the polynuclear structural fragments found wide use as catalysts [1–3] and magnetic [4–6] and luminescent [1, 7] materials. It is difficult to control the composition and structure of the formed polynuclear fragment, which is one of the factors restricting the development of this area of chemistry. A possible solution of this problem is the use as precursors of stable polynuclear blocks, being components of large cluster molecules or coordination polymers. The nature and properties of the blocks weakly depend on crystal field effects. For example, the trinuclear oxometallocarboxylate fragments [8], tetranuclear lithium–zinc complexes [9], tetranuclear copper silsesquioxanes [10], or polyoxometallate compounds [11] are among these structural units. The solid-phase post-synthetic modification of a crystalline complex is a much less abundant method for the controlled change in the composition (more rarely, structure) of polynuclear coordination compounds. At the same time, the "maceration" of a crystal without its dissolution in the active substance can allow one to replace the metal atom itself [12–15], counterion [15, 16], and solvent [17] in the complex, to modify the ligand [18, 19], and finally, to change the dimensionality of the complex (for example, an island complex can be transformed into a coordination polymer) [19, 20]. In addition to a change in the structure, which is accompanied by a change in the properties of the substance, these reactions can provide valuable information about the dynamic behavior of the polynuclear fragment. For instance, the inclusion of a molecule of the solvate component or another active substance into cavities in the crystal or even in the coordination sphere of the complex itself indicates, as a rule, the lability of coordination bonds in the solid phase of the compound [21].

Our attention was attracted by the possibility of modification of the 36-nuclear nickel(II) and cobalt(II) complexes with anions of dimethylmalonic acid using the above method due to the following fac-

tors. On the one hand, exchange interactions between paramagnetic centers of the ferro- and antiferromagnetic type [22, 23] are observed in these compounds. On the other hand, the traditional methods for the synthesis of their analogs are restricted by the replacement of cations, because similar structures have been obtained up to now only for the above indicated metals and only with one of the series of substituted malonic acids [23, 24]. Thus, the purpose of the present work is to check an assumption about the possibility to carry out the post-synthetic modification of crystals of 36-nuclear nickel(II) and cobalt(II) malonates of the discrete structure.

EXPERIMENTAL

The following reagents were used in the work: nickel(II) acetate tetrahydrate (high-purity grade), dimethylmalonic acid (Aldrich, 98%), triethylamine (Acros Organics, 99%), and ethanol (96%). IR spectra were recorded on a PerkinElmer Spectrum 65 instrument using the attenuated total reflectance (ATR) method in a frequency range of 4000–400 cm^{-1}. Elemental analyses were conducted on a EuroEA 3000 CHNS analyzer (EuroVector).

Single crystals of $(NBu_4)_8[Co_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 2.5H_2O \cdot CH_3OH$ (**I**) and $(NBu_4)_8[Ni_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 6H_2O \cdot 2C_2H_5OH$ (**II**) were prepared according to a reported procedure [22].

Synthesis of $(NHEt_3)_3[Ni_{36}(NHEt_3)(H_2O\text{-}\kappa O)_{12.25}\text{-}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_4(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{20}\text{-}(\mu_4\text{-}Me_2Mal)_6] \cdot 39H_2O$ (**III**). Dimethylmalonic acid (0.106 g, 0.80 mmol) was dissolved in ethanol (30 mL), and triethylamine (0.162 g, 1.60 mmol) and nickel(II) acetate (0.200 g, 0.80 mmol) were added. The reaction mixture was stirred on heating ($T = 50°C$) for 1 h. The obtained light green solution was evaporated to half a volume. The formed light green crystals suitable for X-ray diffraction analysis were filtered off and dried in air at 20°C. The yield of compound **III** was 0.027 g (15.7% based on the starting amount of nickel(II)).

For $C_{174}H_{362.5}O_{191.25}Ni_{36}$			
Anal. calcd., %	C, 27.20	N, 0.73	H, 4.75
Found, %	C, 27.43	N, 0.98	H, 4.87

IR (ATR), ν, cm^{-1}: 3540 w, 3388 br.m, 2985 w, 2944 w, 2731 w, 1591 s, 1535 s, 1460 m, 1429 s, 1189 m, 1061 w, 1019 w, 952 w, 936 w, 890 m, 839 m, 788 m, 769 m, 736 s, 706 m, 650 m, 614 s, 590 m, 560 m, 489 m, 459 m, 428 m.

The single crystals obtained from the starting solutions were placed in a solution of 1,4-dioxane (hard Lewis base) or in a 0.1 M solution of Dabco (soft Lewis base) in ethanol and kept at room temperature for a week. The reaction course was monitored by X-ray diffraction analysis.

X-ray diffraction analysis. It was confirmed by the X-ray diffraction analysis before the solid-phase reaction onset that the compositions and structures of compounds **I** and **II** coincided with the earlier reported data. Compound **III** was synthesized for the first time. Intensities of reflections for this complex were measured at the K4.4 BELOK station of the Kurchatov Synchrotron Radiation Source (Kurchatov Institute Russian Research Center, Moscow, Russia) ($\lambda = 0.9699$ Å, RAYONIX CCD 165 detector). An absorption correction was applied empirically using the SCALA program [25]. According to the obtained data, 1,4-dioxane replaces the solvate water and methanol molecules from the single crystal of compound **I** to form $(NBu_4)_8[Co_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{24}(\mu_4\text{-}Me_2Mal)_6] \cdot 7C_4H_8O_2$ (**IV**). The experimental array of reflections was obtained on a Bruker APEX II diffractometer (two-coordinate CCD detector, MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). An absorption correction was applied empirically using the SADABS program [26]. The structures of compounds **III** and **IV** were solved using the SHELXT program [27]. All non-hydrogen atoms were localized from the difference Fourier maps and refined for F^2_{hkl} (SHELXL-14 [28] and OLEX2 [29]). Non-hydrogen atoms of the polynuclear anion, except for the carbon atoms of two methyl groups in compound **III** and one oxygen atom in compound **IV**, were refined in the anisotropic approximation. The non-hydrogen atoms of the cations and solvent molecules were refined in the isotropic approximation. In the case where the equivalent thermal parameters of non-hydrogen atoms exceeded 0.12, their values were fixed. The DFIX and EADP instructions were also used for the refinement of cations. The use of the SQUEEZE/PLATON program [30] indicated a possible presence of two additional nonlocalized 1,4-dioxane molecules in the crystal of compound **IV** (the free volume was 165 $Å^3$ per 46 *e*), whereas the volume of other cavities, which can be attributed to thermal vibrations of the alkyl groups of the cations, did not exceed 20 $Å^3$. In the crystal of compound **III**, the absence of cavities with the volume >50 $Å^3$ and a non-zero number of electrons falling onto these cavities also indicated in favor of a satisfactory quality of the models. Hydrogen atoms were found geometrically and refined in the isotropic approximation in the rigid body model with $U_{iso}(H) = 1.5U_{eq}(X_i)$ for atoms of the methyl groups or $1.2U_{eq}(X_i)$ for other atoms, where $U_{eq}(X)$ are the equivalent thermal parameters of the atoms to which the hydrogen atom was bonded.

The crystallographic characteristics and details of the diffraction experiment are presented in Table 1. The coordinates of atoms, the values of thermal parameters, and the list of all reflections for the studied structures were deposited with the Cambridge

Table 1. Crystallographic data and the experimental and refinement parameters for the structures of compounds **III** and **IV**

Parameter	Value	
	III	**IV**
Empirical formula	$C_{174}H_{362.5}N_4O_{191.25}Ni_{36}$	$C_{306}H_{568}N_8O_{166}Co_{36}$
FW	7688.75	9137.13
T, K	100	120
Crystal system	Cubic	Monoclinic
Space group	$Pm\bar{3}n$	$P2_1/c$
Z	2	2
a, Å	25.444(3)	22.140(3)
b, Å	25.444(3)	25.632(3)
c, Å	25.444(3)	42.332(5)
β, deg	90	122.441(3)
V, Å^3	16473(6)	20274(4)
ρ_{calcd}, g cm^{-3}	1.550	1.497
μ, cm^{-1}	46.22	15.17
F(000)	7945	9520
$2\theta_{max}$, deg	71	52
Number of measured reflections	64376	224704
Number of independent reflections	3240	61986
Number of reflections with $I > 2\sigma(I)$	2694	26787
Number of refined parameters	175	1891
R_1, wR_2 ($I > 2\sigma(I)$)	0.0882, 0.2078	0.1291, 0.2429
R_1, wR_2 (for all data)	0.0971, 0.2128	0.2598, 0.2923
Goodness-of-fit	1.167	1.114
Residual electron density (max/min), *e* Å^{-3}	−2.680/6.534	−1.907/3.405

Crystallographic Data Centre (CIF files CCDC no. 1557499 (**III**) and 1557500 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The single crystals of compounds **I**–**III** are completely dissolved in a 0.1 M solution of Dabco in ethanol. On the contrary, the system remains heterogeneous for a prolonged time upon the interaction of the single crystals of compounds **I** and **II**, whereas complex **III** is also dissolved, probably, due to a high content of water molecules in the cell. At the same time, the responses of compounds **I** and **II** to this solvent also differ. Nickel-containing complex **II** decomposes to a powder, the structure of which cannot be established even using highly intense X-ray radiation sources. The single crystal of cobalt-containing compound **I** remains suitable for X-ray diffraction analysis, although its quality is somewhat decreased compared to the starting single crystal, which is seen from the high *R* factors. At the same time, all solvent molecules were unambiguously revealed in the difference electron density syntheses and refined, except for one 1,4-dioxane molecule of four independent ones, without geometric constraints, whereas the constraints of bond lengths and bond angles were used for the refinement of positions of the cations.

The crystals of compounds **I** and **IV** can be considered isostructural ignoring solvated molecules, since the space group remains unchanged and the parameters of the unit cell and positions of the anions are similar in both crystals. The independent part of the cell contains half an anion, four cations, and four dioxane molecules. On going from compound **I** to compound **IV**, the volume of the crystal increases insignificantly (by 0.7%), although the compositions of the solvate moiety ($2.5H_2O \cdot CH_3OH$ and $7C_4H_8O_2$, respectively) differ noticeably in the number of non-hydrogen atoms. This became possible, most likely, due to a more ordered (in the case of compound **IV**) arrangement of the alkyl groups of the tetrabutylammonium cations. According to the obtained data, the composi-

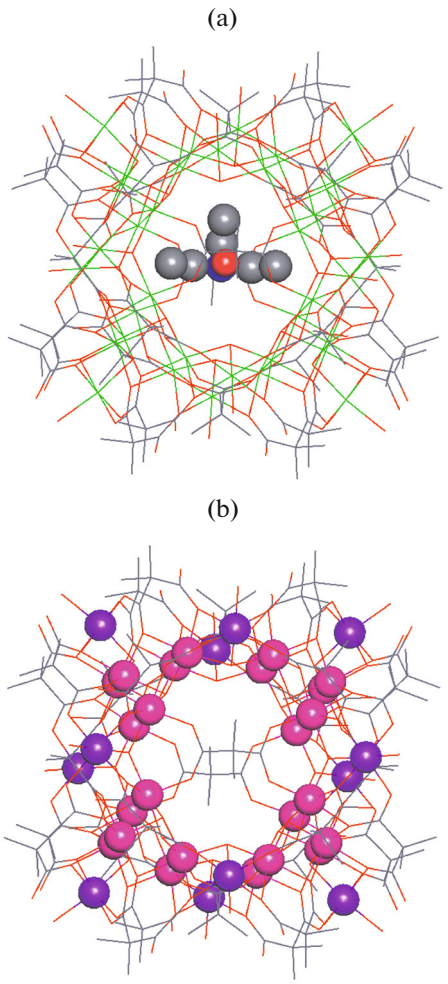

Fig. 1. Molecular structures of the polynuclear anions in compounds (a) **III** and (b) **IV**. The position of the water molecule and one of the positions of triethylammonium encapsulated inside the anionic framework are shown by the ball-and-stick model in Fig. 1a. The positions of the metal atoms ("external" atoms are darker than "internal" ones) are shown in Fig. 1b.

tion and structure of the framework of the anionic complex remain unchanged. As in the starting compound [22] or earlier obtained salts [23, 24], the anionic complex contains 36 metal atoms (24 "internal" and 12 "external"), six tetradentate μ_4-bridging and 24 tridentate μ_4-bridging dimethylmalonate anions, and, in addition, μ_3-bridging hydroxo groups, the hydrogen atoms in which are directed inside the polynuclear cation, as well as water molecules coordinated by the "external" cobalt(II) atoms (Fig. 1b). Although the volume of the internal cavity is ~150 Å^3, the intensity of the molybdenum source of X-ray radiation is probably insufficient for the evaluation of the presence of encapsulated molecules or ions. This conclusion can be drawn due to the first X-ray diffraction analysis of 36-nuclear dimethyl malonates performed using synchrotron radiation. The data obtained show that the structure of compound **III** exhibits the difference electron density peaks inside the anionic framework interpreted as a partially populated position of the water molecule rigidly at the center of the cavity and disordered by symmetry over 12 positions of the triethylammonium cation (Fig. 1a). Since the shortest N(1)···O(8) distance between the nitrogen atom of the encapsulated cation and oxygen of the anionic framework is 3.369(1) Å, it can be assumed that the cation is involved in intramolecular hydrogen bonds. Also note that the anionic framework can encapsulate potassium cations [23] but lighter atoms can be localized inside the cavity probably only using highly intense radiation sources as confirmed previously. In addition to the already considered cation, the structure of compound **III** contains three out-of-sphere triethylammonium cations also disordered over several positions. Other single peaks of the difference electron density were interpreted as belonging to water molecules. Therefore, the anionic complex contains four "acidic" HMe_2Mal^- anions along with the Me_2Mal^{2-} anions.

The change in the structure from compound **I** to **IV** upon the replacement of the out-of-sphere molecules is shown in Fig. 2, which clearly demonstrates that the centers of gravity of the anionic polynuclear complexes and their arrangement and shape in the structure remain unchanged. Although the X-ray diffraction data confirm that the crystals of compound **IV** contain eight cations per anion, it is also demonstrated in Fig. 2 that the positions of only some of them (designated as Cat1) remain close to the position of the initial cations. Other cations (Cat2) undergo either a significant change in the conformation of the butyl fragment, or even the shift of the whole cation induced by the substitution of the solvate water and ethanol molecules by 1,4-dioxane molecules. Although it is impossible to evaluate the presence of the latter in the cavity of the polynuclear anion, it can unambiguously be established that 1,4-dioxane can "percolate" inside the single crystals of the polynuclear *d*-metal complexes with the malonic acid derivatives of the discrete structure without its dissolution (this is also indicated by the dissolution of nickel complex **II**), in spite of the fact that 1,4-dioxane does not displace water molecules from the coordination sphere of the cobalt(II) atoms. This fact indicates that 1,4-dioxane can further be used as a polar solvent for other N- or O-donor molecules, which could displace water molecules from the coordination sphere of the metal atoms and act as linkages of anionic complexes.

To conclude, it is established that the modification of the 36-nuclear 3*d*-metal complexes with anions of substituted malonic acids with the discrete structure is possible in the solid-phase reactions but requires a careful choice of the solvent that would not decompose the single crystal. The interpretation of the results can be impeded by worsening of single crystal quality

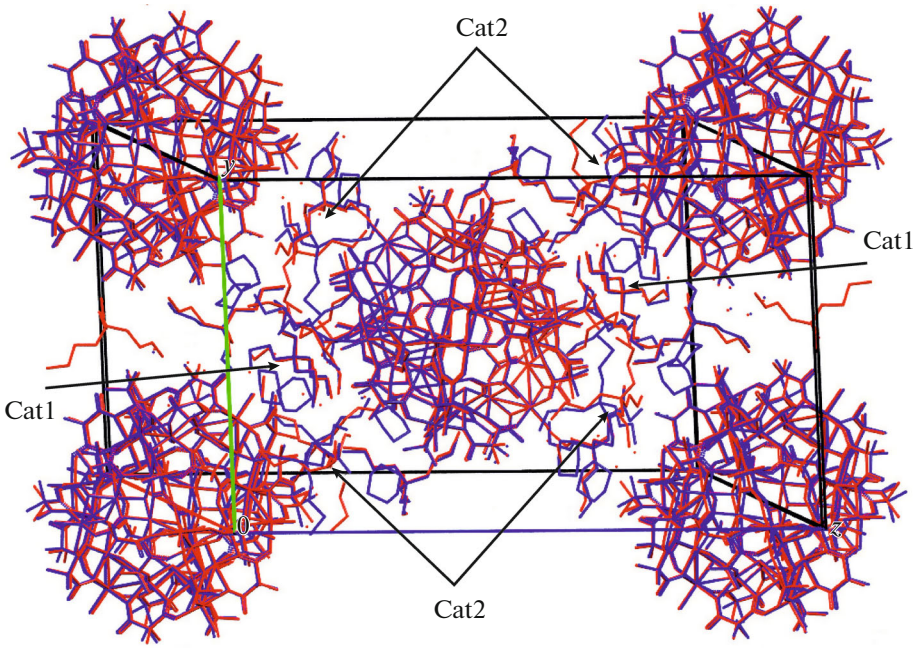

Fig. 2. Packing fragments of compounds **I** and **II** when superimposing the unit cells. Hydrogen atoms are omitted; and Cat1 and Cat2 designate the cations that undergo no noticeable shift and conformational changes in the course of the solid-phase reaction.

and needs the application of highly intense X-ray radiation sources or the use of additional physicochemical methods.

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