ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 3, pp. 180–185. © Pleiades Publishing, Ltd., 2021.
Russian Text © The Author(s), 2021, published in Koordinatsionnaya Khimiya, 2021, Vol. 47, No. 3, pp. 153–158.

36-Nuclear Coordination Compounds of Nickel(II) with Malonate Anions and Internal Aquated Magnesium and Sodium Cations

E. N. Zorina-Tikhonova[a, *], A. V. Vologzhanina[b], K. A. Babeshkin[a], N. N. Efimov[a], P. V. Dorovatovskii[c], M. A. Kiskin[a], A. A. Sidorov[a], and I. L. Eremenko[a, b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *Nesmeyanov Institute of Orgaìnoelement Compounds, Russian Academy of Sciences, Moscow, Russia*
[c] *National Research Center Kurchatov Institute, Moscow, Russia*
**e-mail: ezorinatikhonova@gmail.com*

Received October 15, 2020; revised October 20, 2020; accepted October 21, 2020

Abstract—The new anionic dimethylmalonate complex $\{Ni_{36}(H_2O)_{12}(OH)_{20}(HMe_2Mal)(Me_2Mal)_{29}@[Mg(H_2O)_6]\}^{5-}$ (Me_2Mal^{2-} is the dimethylmalonate anion) containing the internal aquated $[Mg(H_2O)_6]^{2+}$ ion and the external $[Mg_3(OH)(H_2O)_{10}(C_2H_5OH)_3]^{5+}$ cation was prepared by hydrothermal synthesis. The crystalline compound isolated from the reaction mixture and characterized by X-ray diffraction had the formula $[Mg_3(OH)(H_2O)_{10}(C_2H_5OH)_3]\{Ni_{36}(H_2O)_{12}(OH)_{20}(HMe_2Mal)(Me_2Mal)_{29}@[Mg(H_2O)_6]\}\cdot 25H_2O$ (**I**) (CIF file CCDC no. 2038910). The new anionic complex $\{Ni_{36}(H_2O)_{12}(OH)_{19}(O)(Cbdc)_{30}@[Na(H_2O)_6]\}^{8-}$ ($Cbdc^{2-}$ is the cyclobutane-1,1-dicarboxylate anion) containing the internal aquated $[Na(H_2O)_6]^+$ ion and outer-sphere tetrabutylammonium cations was prepared from an ethanol–acetonitrile solution. The crystals isolated from the reaction mixture were characterized by X-ray diffraction and were described the formula $(NBu_4)_8\{Ni_{36}(H_2O)_{12}(OH)_{19}(O)(Cbdc)_{30}@[Na(H_2O)_6]\}$ (CIF file CCDC no. 2038909) (**II**). It was found that the magnetic behavior of complex **I** is due to competing ferro- and antifferromagnetic exchange interactions between paramagnetic nickel(II) ions.

Keywords: polynuclear *d*-metal complexes, nickel(II) carboxylates, dimethylmalonates, cyclobutane-1,1-dicarboxylates

DOI: 10.1134/S1070328421030088

INTRODUCTION

Previously, we showed that the synthesis of homometallic nickel(II) compounds with dimethylmalonic acid anions and organic cations (triethylammonium, tetrabutylammonium) gives molecular spherical 36-nuclear polyanionic compounds [1, 2]. The use of potassium together with 18-crown-6 or silver(I) as the cations results in the formation of polymeric compounds [3, 4]. In the potassium-containing compound, 36-nuclear polyanion is the primary unit [3], while in the case of silver(I), a 2D structure based on bis-chelate $\{Ni(Me_2Mal)_2\}^{2-}$ fragments, $[Ag2Ni(H_2O)_2(Me_2Mal)_2]n$, is formed [4]. There are known heterometallic nickel(II) complexes with cyclobutane-1,1-dicarboxylic acid (H_2Cbdc) anions: a layered Ni(II)–Ag(I) polymer, an analogue of the above-mentioned 2D polymer [4], the ionic complex $[Ni(H_2O)_6][Cu(Cbdc)_2(H_2O)]$, and 1D polymer $[Ni(VO)(Cbdc)_2(EtOH)_2(H_2O)_3]_n$ [5].

In this study, we describe various methods of chemical engineering of polynuclear carboxylate anionic fragments containing nickel(II), sodium, or magnesium ions and dimethylmalonic (H_2Me_2Mal) or cyclobutane-1,1-dicarboxylic acid (H_2Cbdc) dianions. The structure and magnetic behavior (for the dimethylmalonate derivative) of these compounds were studied and the effect of differently charged internal $[M(H_2O)_6]^{n+}$ cations ($n = 1$ or 2) on the structure of the $\{Ni_{36}\}^{n-}$ anions was considered.

EXPERIMENTAL

Complexes **I** and **II** were synthesized in air using ethanol (96%), acetonitrile (99%), distilled water, and commercially-available $NiSO_4\cdot 6H_2O$ (Chimmed, high-purity grade), $Ni(OAc)_2\cdot 4H_2O$ (Riedel-de-Haën, 98%), $MgSO_4\cdot 7H_2O$ (Reachem, high-purity grade), $Ba(OH)_2\cdot H_2O$ (Sigma-Aldrich, 98%), NBu_4OH (40% aqueous solution, Alfa Aesar), NaOH (Chimmed, high-purity grade), H_2Me_2Mal (Sigma-Aldrich, 98%), and H_2Cbdc (Sigma-Aldrich, 99%).

Synthesis of $[Mg_3(OH)(H_2O)_{10}(C_2H_5OH)_3]$-$\{Ni_{36}$-$(H_2O$-$\kappa O)_{12}(\mu_3$-$OH)_{20}(\mu_4$-$HMe_2Mal$-$\kappa^2O,O')$-$(\mu_4$-$Me_2Mal$-$\kappa^2O,O')_{23}(\mu_4$-$Me_2Mal)_6$@$[Mg(H_2O)_6]\}\cdot 25H_2O$ (I). Weighed portions of $NiSO_4\cdot 6H_2O$ (0.187 g, 0.7 mmol), $MgSO_4\cdot 7H_2O$ (0.175 g, 0.7 mmol), H_2Me_2Mal (0.188 g, 1.4 mmol), and $Ba(OH)_2\cdot H_2O$ (0.269 g, 1.4 mmol) in a water-ethanol mixture (5/2 mL) were charged into an autoclave reactor with a Teflon insert. The $BasSO_4$ residue was preliminarily filtered. The mixture was kept for 72 h at 100°C. The light green crystals suitable for X-ray diffraction were separated from the mother liquor by decantation, washed with cold EtOH, and dried in air. The yield of compound **I** was 0.045 g (31% based on the initial amount of nickel(II)).

For $C_{144}H_{356}Ni_{36}O_{197}Mg_4$ ($M = 7451.09$)

Anal. calcd., %	C, 23.21	H, 4.82
Found, %	C, 23.45	H, 5.01

IR spectrum (ATR; ν, cm^{-1}): 3540 m, 3365 m, 2983 m, 2944 w, 1589 s, 1534 s, 1461 s, 1430 s, 1345 s, 1189 m, 1138 m, 936 w, 893 m, 840 m, 787 m, 732 s, 614 s, 559 m, 500 m, 458 s, 444 s, 430 s.

Synthesis of $(NBu_4)_8\{Ni_{36}(H_2O)_{12}(\mu_3$-$OH)_{19}(\mu_3$-$O)(\mu_4$-$Cbdc$-$\kappa^2O,O')_{24}(\mu_4$-$Cbdc)_6$@$[Na(H_2O)_6]\}$ (II). Weighed portions of a 40% aqueous solution of tetrabutylammonium hydroxide (3.120 g of the solution, 4.8 mmol) and H_2Cbdc (0.347 g, 2.4 mmol) were dissolved in ethanol, and $Ni(OAc)_2\cdot 4H_2O$ (0.30 g, 1.2 mmol) and NaOH (0.01 g, 0.25 mmol) were added. The reaction mixture was stirred with heating ($T = 50$°C) for 1 h. The resulting light green solution (45 mL) was concentrated to 20 mL, added acetonitrile (10 mL), and the mixture was kept in air at 20°C. The crystals of **II** suitable for X-ray diffraction, which formed in 24 h, were separated on a filter and dried in air at $T = 20$°C. The yield of **II** was 0.057 g (19% based on the initial amount of nickel(II)).

For $C_{308}H_{523}N_8O_{158}NaNi_{36}$ ($M = 9002.86$)

Anal. cald., %	C, 41.09	H, 5.86	N, 1.24
Found, %	C, 41.23	H, 5.96	N, 1.43

IR spectrum (ATR; ν, cm^{-1}): 3544 m, 2963 m, 2941 m, 2876 w, 1594 s, 1548 s, 1450 s, 1413 s, 1355 s, 1257 m, 1242 m, 1167 m, 1099 m, 1015 m, 948 m, 903 m, 854 m, 798 m, 751 c, 683 m, 633 m, 533 m, 479 m, 460 m, 417 s.

X-ray diffraction. The experimental set of reflections for complex **I** was collected on a Bruker APEX II diffractometer (CCD array detector, MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The absorption corrections were applied empirically by the SADABS program package [6]. The structures were solved using the SHELXT program package [7]. All non-hydrogen atoms were located from difference electron density maps and refined on F^2_{hkl} (SHELXL-14 [8] and OLEX2 [9]). The set of reflections for complex **II** was collected on the K4.4 BELOK station of the Kurchatov Center for Synchrotron Radiation (National Research Center Kurchatov Institute, Moscow, Russia) ($\lambda = 0.9699$ Å, RAYONIX CCD 165 detector) at 100.0(2) K. The absorption corrections were applied empirically using the SCALA program [10].

Except for two methyl groups in **I** and four disordered cyclobutane groups in **II**, the non-hydrogen atoms of the polynuclear anion were refined in the anisotropic approximation. Also, the SIMU, ISOR, and EADP commands were used to refine the thermal parameters of some atoms in **I**; DFIX, RIGU, and EADP commands were used to refine the cations and disordered anions in **II**. The 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 methyl groups and water molecules and $U_{iso}(H) = 1.2U_{eq}(X_i)$ for other atoms, where $U_{eq}(X)$ are equivalent thermal parameters of atoms bearing the hydrogen atoms. The structure of **I** contains disordered solvent molecules, the contribution of which to the reflection intensities was estimated by the SQUEEZE/PLATON program [11].

The crystallographic characteristics and X-ray experiment details are summarized in Table 1.

The atom coordinates, thermal parameters, and the list of all reflections for the studied structures are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2038910 (**I**), 2038909 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/structures).

The magnetic behavior of complex **I** was investigated by static magnetic susceptibility measurements on a PPMS-9 magnetometer (QuantumDesign) in the range of 2–300 K in a 5 kOe static magnetic field. All magnetic behavior measurements were carried out for a ground polycrystalline sample sealed in a plastic bag and frozen in mineral oil to prevent the orientation of crystallites in a magnetic field. The paramagnetic component of the magnetic susceptibility (χ) was determined considering the diamagnetic contributions of the sample, mineral oil, and the holder.

RESULTS AND DISCUSSION

The crystals of $[Mg_3(OH)(H_2O)_{10}(C_2H_5OH)_3]$-$\{Ni_{36}(H_2O$-$\kappa O)_{12}(\mu_3$-$OH)_{20}(\mu_4$-$HMe_2Mal$-$\kappa^2O,O')$-$(\mu_4$-$Me_2Mal$-$\kappa^2O,O')_{23}(\mu_4$-$Me_2Mal)_6$@$[Mg(H_2O)_6]\}\cdot 25H_2O$ (**I**) were prepared by the hydrothermal synthesis, while the crystals of complex $(NBu_4)_8\{Ni_{36}$-$(H_2O)_{12}(\mu_3$-$OH)_{19}(\mu_3$-$O)(\mu_4$-$Cbdc$-$\kappa^2O,O')_{24}(\mu_4$-$Cbdc)_6$@$[Na(H_2O)_6]\}$ (**II**) were obtained by crystallization in air.

Table 1. Crystallographic data X-ray diffraction experiment and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
T, K	120	100
System	Cubic	Monoclinic
Space group	$Pm\bar{3}n$	$P2_1/c$
Z	2	2
a, Å	25.4062(6)	23.060(5)
b, Å	25.4062(6)	26.521(5)
c, Å	25.4062(6)	35.047(5)
β, deg	90	92.23(3)
V, Å^3	16399(1)	21417(7)
ρ(calcd.), g cm^{-3}	1.510	1.395
μ, cm^{-1}	21.16	35.65
F(000)	7710	9408
$2\theta_{max}$, deg	59	77
Number of measured reflections	87919	200691
Number of unique reflections	3828	44897
Number of reflections with $I > 2\sigma(I)$	2758	23377
Number of refined parameters	219	2218
R_1, wR_2 ($I > 2\sigma(I)$)	0.0830, 0.2023	0.1013, 0.1842
R_1, wR_2 (for all data)	0.1151, 0.2200	0.1822, 0.2120
GOOF	1.240	1.208
Residual electron density (min/max), e Å^{-3}	−2.797/2.774	−1.226/2.549

According to X-ray diffraction data, compounds **I** and **II**, like previously studied polynuclear nickel(II) and cobalt(II) dimethylmalonates, contain 36 metal atoms (24 internal and 12 external ones), six tetradentate μ_4-bridging and 24 tridentate μ_4-bridging malonate anions, μ_3-bridging hydroxy groups, with their hydrogen atoms pointing inside the polynuclear anion, and water molecules coordinated by the external metal(II) ions (Fig. 1) [1–3, 12]. It should be noted that compound **II** indicates directly that polyanionic 36-nuclear carboxylate compounds containing 3d metal ions (at least Co(II) and Ni(II)) and substituted malonate anions are characteristic of not only dimethylmalonate derivatives, but also other malonate anions, for example, cyclobutane-1,1-dicarboxylate.

The unit cell of compound **I** is similar to that of previously obtained nickel(II) complex with dimethylmalonate anions and triethylammonium cations $(NHEt_3)_3[Ni_{36}(H_2O)_{12.25}(OH)_{20}(HMe_2Mal)_4(Me_2Mal)_{20}(Me_2Mal)_6@(NHEt_3)]\cdot 39H_2O$ (space group $Pm\bar{3}m$, $a = b = c \approx 25.4$ Å [1]). In both cases, the independent part of the unit cell contains two independent metal atoms, 1.5 independent dicarboxylate anions, two hydroxy anions, and a water molecule, and also encapsulated and outer-sphere cations and uncoordinated water molecules. Meanwhile, the structures of cations, which formally occupy equivalent positions, are substantially different. The electron density inside the anion in **I** can be interpreted as the $[Mg(H_2O)_6]^{2+}$ cation disordered over four positions due to high crystal symmetry and participating in hydrogen bonding with the oxygen atoms of dimethylmalonate anions, which form the inner cavity.

Determination of the chemical composition of the outer-sphere cation is complicated by the fact that it is located in a special position. The electron density in the (0.75 : 0.5 : 0) position, which can be considered to be an oxygen atom, is surrounded by four heavier atoms spaced 1.98(1) Å apart and bound, in turn, to several other light atoms. Thus, the central fragment of the cation can be identified as the tetranuclear $[Mg_4(\mu_4\text{-}O)]^{6+}$ cation or trinuclear $[Mg_3(\mu_3\text{-}O)]^{4+}$, $[Mg_3(\mu_3\text{-}OH)]^{5+}$, or $[Mg_3(\mu_3\text{-}H_2O)]^{6+}$ cation disordered over four positions. The electroneutrality reasons attest in favor of hexacations. However, the tetranuclear $[Mg_4(\mu_4\text{-}O)]^{6+}$ cations, structurally characterized previously, have a tetrahedral arrangement of metal atoms centered by the oxo anion, while in the

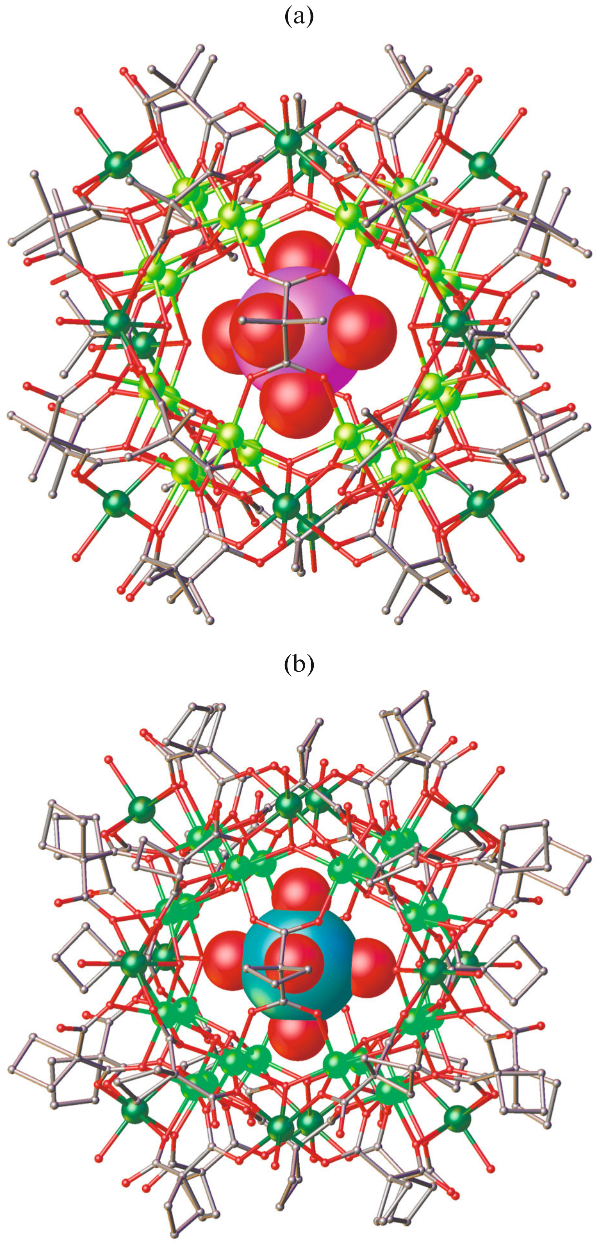

Fig. 1. Molecular structure of polynuclear anions in **I** (a) and **II** (b). The hydrogen atoms are omitted, the external metal atoms are darker than the internal ones. The encapsulated cations (one of the positions of $[Mg(H_2O)_6]^{2+}$(a); $[Na(H_2O)_6]^+$(b)) are shown as van der Waals spheres.

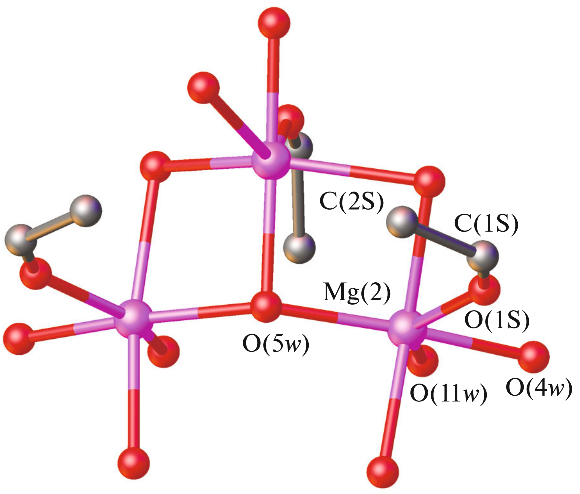

Fig. 2. Structure of the $[Mg_3(OH)(H_2O)_{10}(C_2H_5OH)_3]^{5+}$ cation in **I**.

considered structure, the metal atoms are located at the vertices of a bisphenoid. In the case of a trinuclear cation, refinement with a partially occupied position of magnesium gives lower *R*-factors and the thermal ellipsoids of metal atoms close to those of carbon and oxygen atoms in this structure. Generally, the trinuclear cation has a triangular arrangement of metal atoms with a bridging oxygen atom located above their plane. The coordination environment of magnesium is supplemented by a terminal ethanol molecule and four water molecules (Fig. 2). According to X-ray diffraction data, the presumed composition of the outer-sphere cation is $[Mg_3(\mu_3\text{-}H_2O)(\mu_2\text{-}H_2O)_2(H_2O)_8\text{-}(C_2H_5OH)_3]^{6+}$ or $[Mg_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)_2(H_2O)_8\text{-}(C_2H_5OH)_3]^{5+}$. In the latter case, it is hardly possible to find out which of the OH groups of the polynuclear anion acquires a proton to become a water molecule; however, X-ray diffraction data for complex **I** and for previously synthesized 36-nuclear nickel(II) compounds [1–3] also indicate that the charge of the anion can vary.

Complex **II** crystallizes in the monoclinic system; the independent part of the unit cell contains half of the anion and four outer-sphere tetrabutylammonium cations, similarly to most of the previously obtained complexes. The inner cavity of the anion contains the encapsulated $[Na(H_2O)_6]^+$ cation, which is involved in hydrogen bonding with six μ_4-bound H_2Cbdc anions (Fig. 3); thus, the $[An]^{8-}$ charge can be ascribed to the anion, taking account of the encapsulated cation ($[An@[Na(H_2O)_6]]^{8-}$). The bond lengths in the hexaaqua cation vary from 2.308(10) to 2.333(9) Å, and the angles vary in the 87.0(5)°–91.0(5)° range.

For compound **I**, magnetic measurements were carried out in the temperature range of 2–300 K in a 5 kOe magnetic field. The $\chi_M T$ value for **I** at 300 K, amounting to 39.0 cm^3 K mol^{-1}, corresponds to the value expected for 36 non-interacting nickel(II) ions with the spin $S = 1$ and $g = 2.08$. As the temperature decreases, $\chi_M T$ monotonically increases to a maximum of 87.9 cm^3 K mol^{-1} at 6 K, while further decrease in the temperature is accompanied by a sharp decrease in $\chi_M T$, with the minimum value being 46.5 cm^3 K mol^{-1} at 2 K (Fig. 4). This magnetic behavior in the 300–6 K range is due to the predominant ferro-

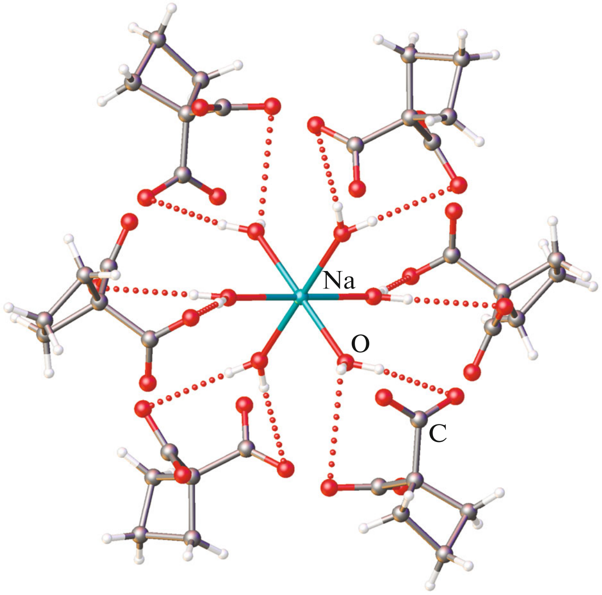

Fig. 3. Hydrogen bonds between the encapsulated $[Na(H_2O)_6]^+$ cation and the polynuclear anion in **II**.

magnetic exchange interactions between the nickel(II) ions in $\{Ni_3(\mu_3\text{-}OH)(\mu\text{-}OR)_3\}$, which was previously shown for molecular nickel(II) complexes [13–21]. The decrease in $\chi_M T$ is attributable to antiferromagnetic exchange and the Zeeman effect. The course of the $\chi_M T(T)$ curve coincides with that described previously for the complex $(NBu_4)_8[Ni_{36}(H_2O)_{12}(OH)_{20}(Me_2Mal)_{30}]\cdot 6H_2O\cdot 2EtOH$, in which there are no inner cation insertions [2] and for which the magnitudes of exchange interactions have been determined.

Thus, we prepared new anionic nickel(II) carboxylate complexes with a 36-nuclear metal core and internal aquated cations with different charges. Presumably, irrespective of the method of synthesis (hydrothermal or solution) and of the nature of carboxylate dianions (Me_2Mal^{2-} or $Cbdc^{2-}$), the formation of species of this type would also be quite likely in other similar reaction systems. The presence of a cavity in the 36-nuclear polyanions allows encapsulation of aquated sodium or magnesium cations or solvent molecules, which is confirmed by single crystal X-ray diffraction experiments.

ACKNOWLEDGEMENTS

IR spectroscopy and elemental analysis were carried out using the research equipment of the JRC PMR of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, which is supported by the state assignment for the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of fundamental research. The X-ray diffraction data for complex **I** were obtained using the equipment of the Center for Structural Investigations of the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

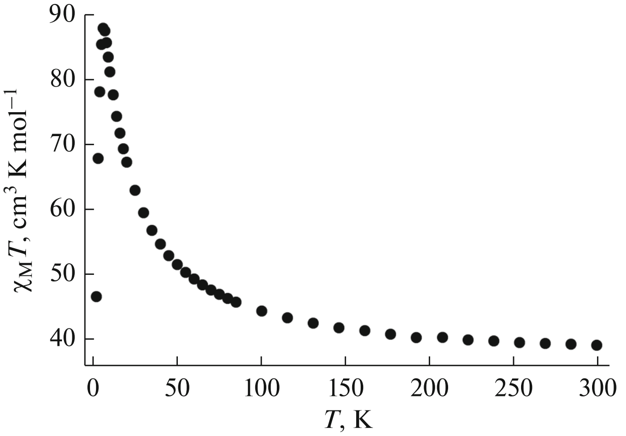

Fig. 4. Temperature dependence of $\chi_M T$ of complex **I** in a 5 kOe static magnetic field in the 2–300 K range.

FUNDING

This study was supported by the Russian Science Foundation (project no. 19-73-10181).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Vologzhanina, A.V., Zorina-Tikhonova, E.N., Matyukhina, A.K., et al., *Russ. J. Coord. Chem.*, 2017, vol. 43, p. 801. https://doi.org/10.1134/S1070328417120107
2. Zorina-Tikhonova, E.N., Gogoleva, N.V., Sidorov, A.A., et al., *Polyhedron*, 2017, vol. 130, p. 67.
3. Zorina-Tikhonova, E.N., Gogoleva, N.V., Sidorov, A.A., et al., *Russ. Chem. Bull.*, 2015, vol. 64, p. 636.
4. Zorina-Tikhonova, E.N., Gogoleva, N.V., Aleksandrov, E.V., et al., *Russ. Chem. Bull.*, 2016, vol. 6, p. 759.
5. Bazhina, E.S., Gogoleva, N.V., Aleksandrov, G.G., et al., *Chem. Select.*, 2018, vol. 3, p. 13765.
6. Sheldrick, G.M., *SADABS. Program for Empirical X-ray Absorption Correction*, Bruker-Nonius, 1990–2004.
7. Sheldrick, G.M., *Acta Crystalogr., Sect A: Found. Adv.*, 2015, vol. 71, no. 1, p. 3.
8. Sheldrick, G.M., *Acta Crystalogr., Sect. C: Struct. Chem.*, 2015, vol. 71, no. 1, p. 3.
9. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, no. 2, p. 339.
10. Winn, M.D., Ballard, C.C., Cowtan, K.D., et al., *Acta. Crystallogr., Sect. D: Biol. Crystallogr.*, 2011, vol. 67, no. 4, p. 235.

11. Spek, A.L., *Acta Crystalogr., Sect. C: Struct. Chem.*, 2015, vol. 71, no. 1, p. 9.
12. Zorina, E.N., Zauzolkova, N.V., Sidorov, A.A., et al., *Inorg. Chim. Acta*, 2013, vol. 396, p. 108.
13. Ghosh, A.K., Shatruk, M., Bertolasi, V., et al., *Inorg. Chem.*, 2013, vol. 52, p. 13894.
14. Ferguson, A., Lawrence, J., Parkin, A., et al., *Dalton Trans.*, 2008, no. 45, p. 6409.
15. Costes, J.P., Novitchi, G., Vendier, L., et al., *Comptes Rendus Chimie*, 2012, vol. 15, p. 849.
16. Ghisolfi, A., Monakhov, K.Yu., Pattacini, R., et al., *Dalton Trans.*, 2014, vol. 43, p. 7847.
17. Paine, T.K., Rentschler, E., Weyhermuller, T., and Chaudhuri, P., *Eur. J. Inorg. Chem.*, 2003, p. 3167.
18. Karmakar, S. and Khanra, S., *CrystEngComm*, 2014, vol. 16, p. 2371.
19. Mandal, D., Hong, C.S., Kim, H.C., et al., *Polyhedron*, 2008, vol. 27, p. 2372.
20. Boskovic, C., Rusanov, E., Stoeckli-Evans, H., and Gudel, H.U., *Inorg. Chem. Commun.*, 2002, vol. 5, p. 881.
21. Mukherjee, P., Drew, M.G.B., Tangoulis, V., et al., *Inorg. Chem. Commun.*, 2009, vol. 12, p. 929.

Translated by Z. Svitanko