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Novel polynuclear architectures incorporating Co^{2+} and K^{+} ions bound by dimethylmalonate anions: Synthesis, structure, and magnetic properties

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ABSTRACT

The reaction of potassium dimethylmalonate (K_2Me_2Mal) and cobalt(II) pivalate $[Co(Piv)_2]_n$ under various conditions resulted in $\{[K_2Co(H_2O\text{-}\kappa O)(\mu\text{-}H_2O)(\mu_6\text{-}Me_2Mal)(\mu_5\text{-}Me_2Mal)]\cdot 2H_2O\}_n$ (**1**) and $\{[K_6Co_{36}(H_2O\text{-}\kappa O)_{22}(\mu\text{-}H_2O)_6(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_2(\mu_6\text{-}Me_2Mal\text{-}\kappa^2O,O')_2(\mu_5\text{-}Me_2Mal\text{-}\kappa^2O,O')_8(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{12}(\mu_4\text{-}Me_2Mal)_6]\cdot 58H_2O\}_n$ (**2**) (where Me_2Mal^{2-} is the dimethylmalonate dianion). Coordination polymers **1** and **2** were characterized by X-ray diffraction and magnetochemical studies. Analysis of the magnetic behavior indicates that **1** is characterized by an extremely high anisotropy of magnetic susceptibility and very weak spin coupling between Co^{II} centers through malonate groups; compound **2** contains a highly symmetric, spherical-like Co_{36} metal core that exhibits low magnetic anisotropy and antiferromagnetic interactions between Co^{II} centers. Theoretical aspects of anisotropic magnetic properties of orbitally-degenerate Co^{II} ions in polynuclear cobalt(II) complexes are discussed.

1. Introduction

It is well known that, when polynuclear carboxylate complexes are constructed from malonate anions and transition metal ions, crystallization from water or water–alcohol solutions mainly gives coordination polymers with chain, layer, or frame molecular structures build of the bis-chelating dianion $[M^{II}(Mal)_2]^{2-}$ (M^{II} = Co, Ni, Cu, Zn) (see, for example, [1–7]). No polymeric metal-containing malonate systems incorporating large 3d metal containing fragment as structural units are known to date. A promising synthetic strategy to prepare such coordination compounds is based on the ligand-deficient approach that enforces malonate anions to carry out the bridging functions. In this work, we report the preparation of two novel polymeric malonate cobalt(II) complexes with potassium ions, one of which contains an unusual highly symmetric, spherical-like Co_{36} hexanegative anion that functions as a structure-forming molecular building block. These Co^{II} complexes are structurally and magnetically characterized. We also provide some theoretical analysis of a complicated magnetic behavior of these complexes containing orbitally-degenerate six-coordinate Co^{II} ions with an unquenched orbital momentum.

2. Experimental

2.1. Synthesis

Reagents and solvents were commercial available (Aldrich) and used without further purification. Distilled water was used for the synthesis of new compounds. Polymeric cobalt pivalate $[Co(Piv)_2]_n$ was synthesized according to a known procedure [8]. The K_2Me_2Mal salt was prepared by the neutralization of KOH with H_2Me_2Mal.

2.1.1. $\{[K_2Co(H_2O\text{-}\kappa O)(\mu\text{-}H_2O)(\mu_6\text{-}Me_2Mal)(\mu_5\text{-}Me_2Mal)]\cdot 2H_2O\}_n$ (**1**)

$[Co(Piv)_2]_n$ (0.49 g, 1.89 mmol) was added to a solution of K_2Me_2Mal (obtained from potassium hydroxide (0.42 g, 7.58 mmol) and dimethylmalonic acid (0.5 g, 3.78 mmol)) in EtOH (20 ml). The reaction mixture was stirred with weak heating (t = 50 °C) for 10 min to produce a thick violet precipitate. The precipitate was filtered off, washed with EtOH, and dissolved in H_2O (30 ml). The resulting crimson solution was kept for two weeks under air at room temperature. The resulting violet crystals are suitable for X-ray diffraction analysis. The yield of **1** is 0.64 g (71%). *Anal.* Calc. for $C_{10}H_{20}CoK_2O_{12}$: C, 25.59; H, 4.29. Found: C, 25.71; H, 4.38%. IR spectra, ν/cm^{-1}: 3495 s, 2983 m, 2941 m, 2878 m, 2103 w, 1637 s, 1607 s, 1549 s, 1478 s, 1464 m, 1441 s, 1384 m, 1357 m, 1343 s, 1207 m, 1184 m,

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1173 m, 1017 w, 966 w, 892 m, 844 m, 798 w, 782 w, 702 m, 580 m, 533 m, 476 m.

2.1.2. $\{[K_6Co_{36}(H_2O\text{-}\kappa O)_{22}(\mu\text{-}H_2O)_6(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_2(\mu_6\text{-}Me_2Mal\text{-}\kappa^2O,O')_2(\mu_5\text{-}Me_2Mal\text{-}\kappa^2O,O')_8(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{12}(\mu_4\text{-}Me_2Mal)_6]\cdot 58H_2O\}_n$ (**2**)

$[Co(Piv)_2]_n$ (0.2 g, 0.77 mmol) was added to a solution of K_2Me_2Mal (obtained from potassium hydroxide (0.17 g, 3.04 mmol) and dimethylmalonic acid (0.5 g, 1.52 mmol)) in EtOH (20 ml). The reaction mixture was stirred with weak heating ($t = 50$ °C) for 10 min to produce a thick violet precipitate. The resulting suspension was refluxed for 90 min in a water bath. The precipitate was filtered off, washed with EtOH, and dissolved in H_2O (30 ml). The resulting crimson solution was kept for 4 weeks under air at room temperature. The resulting violet crystals are suitable for X-ray diffraction analysis. The yield of **2** is 0.034 g (19%). *Anal.* Calc. for $C_{150}H_{374}Co_{36}K_6O_{226}$: C, 22.10; H, 4.62. Found: C, 21.9; H, 4.5%. IR spectra, ν/cm^{-1}: 3535 s, 3444 m.w, 2982 m, 2203 w, 1599 s, 1541 s, 1464 s, 1433 s, 1351 s, 1190 m, 935 w, 891 m, 834 m, 790 m, 729 m, 652 m, 610 m, 557 m, 482 w.

2.2. Methods

Elemental analysis of the resulting compounds was carried out with a "Carlo Erba" automatic C,H,N,S-analyzer. IR spectra of the complexes were recorded using a "Perkin Elmer Spectrum 65" instrument in KBr pellets in the frequency range of 4000–400 cm^{-1}. The magnetochemical measurements were performed on a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range of 5–300 K in a magnetic field of up to 5 kOe. The calculated molar magnetic susceptibility χ_M was corrected for the diamagnetic contribution. The effective magnetic moment was calculated by the formula $\mu_{eff} = (8\chi T)^{1/2}$.

2.3. X-ray analysis

X-ray diffraction studies were carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (graphite monochromator, $\lambda = 0.71073$ Å). The experimental set of reflections for complexes **1** and **2** was obtained using the standard method [9]. Semi-empirical absorption corrections for both complexes were applied [10]. The structures of the complexes of interest were solved by direct methods using and refined by the least squares method in anisotropic full-matrix approximation (the positions of hydrogen atoms were fixed with UH = 0.082). Hydrogen atoms were generated geometrically and refined in the "riding" model. All calculations were carried out with the use of the SHELX97 program package [11]. The crystallographic data and the refinement procedure details are given in Table 1. The structure of complex **1** was determined without applying any additional restrictions, except above mentioned restrictions on hydrogens. Some of dimethylmalonate groups in structure **2** are particular unordered, and as result the lengths of similar bond C–O were essentially different. Therefore some of distances in the C–O groups of some dimethylmalonate groups are restrained to a target value d ('free variable'). Additionally also position multiplicity of some atom O of some molecules water were not equal 1.0. And its sites occupation factors reastrained to be constant (usually ~5).

3. Results and discussion

3.1. Synthesis and structure of **1**

We have found that the reaction of polymeric cobalt(II) pivalate $[Co(Piv)_2]_n$ with potassium dimethylmalonate K_2Me_2Mal (where Me_2Mal is the dimethylmalonate dianion) in EtOH ($t = 50$ °C) gives a 2D-polymer $\{[K_2Co(H_2O\text{-}\kappa O)(\mu\text{-}H_2O)(\mu_6\text{-}Me_2Mal)(\mu_5\text{-}Me_2Mal)]\cdot 2H_2O\}_n$ (**1**), which was isolated as violet crystals. According to X-ray diffraction data (Table 1), polymer **1** does not incorporate the well-known six-membered chelate rings with metal centers (Fig. S1) typical of structural units in this kind of systems, which is unusual for polymeric coordination malonates with transition metal atoms in the absence of additional N-donor ligands [12,13].

Table 1
Crystal data and structure refinement for **1** and **2.**

Compound	**1**	**2**
Formula	$C_{10}H_{20}CoK_2O_{12}$	$C_{150}H_{374}Co_{36}K_6O_{226}$
Formula weight (g mol^{-1})	469.39	8150.67
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.486(3)	22.053(1)
b (Å)	10.694(4)	28.8254(14)
c (Å)	11.541(4)	24.7174(12)
α (°)	74.122(5)	90.00
β (°)	68.625(5)	90.0248(8)
γ (°)	68.974(5)	90.00
V (Å^3)	898.0(6)	15712.5(13)
Z	2	2
Absorption coefficient (mm^{-1})	1.479	2.04
Maximum and minimum transmission	0.866/0.930	0.553/0.822
D_{calc} (mg/m^3)	1.784	1.733
Crystal size (mm)	0.10 × 0.05 × 0.05	0.33 × 0.14 × 0.10
θ (°)	2.58–30.34	2.3–25.5
Reflection measured	9332	144142
Reflection unique	3715	26388
R_{int}	0.0252	0.0634
Goodness-of-fit (GOF) on F^2	1.053	0.998
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0302$, $wR_2 = 0.0735$	$R_1 = 0.0683$, $wR_2 = 0.1887$
R indices (all data)	$R_1 = 0.0361$, $wR_2 = 0.0760$	$R_1 = 0.0884$, $wR_2 = 0.2121$

The octahedral environment of cobalt(II) ions in structure **1** (Fig. 1) formally consists of O atoms of four carboxylate groups, two of which belong to different dianions from two four-membered chelate fragments CoO_2C, whereas the two remaining O atoms belong to two other dianions (Table 2).

3.2. Synthesis and structure of **2**

It has been found that prolonged refluxing of a suspension of compound **1** in EtOH (90 min) gives a new coordination polymer $\{[K_6Co_{36}(H_2O\text{-}\kappa O)_{22}(\mu\text{-}H_2O)_6(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_2(\mu_6\text{-}Me_2Mal\text{-}\kappa^2O,O')_2(\mu_5\text{-}Me_2Mal\text{-}\kappa^2O,O')_8(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{12}(\mu_4\text{-}Me_2Mal)_6]\cdot 58H_2O\}_n$ (**2**), in which the $\{[Co_{36}(H_2O\text{-}\kappa O)_{12}(\mu_3\text{-}OH)_{20}(\mu_4\text{-}HMe_2Mal\text{-}\kappa^2O,O')_2(\mu_4\text{-}Me_2Mal\text{-}\kappa^2O,O')_{22}(\mu_4\text{-}DMM)_6]\}_n^{6-}$ 36-nuclear hexanegative anion interlinked by potassium cations are the main structural units (Fig. 2).

The $\{Co_{36}\}^{6-}$ hexanegative anion is located in the crystallographic center of symmetry. It should be noted that one of the three independent potassium cations in the unit cell is disordered and occupies two positions with ~1/2 population. A fraction of the malonate ligands are also disordered; the O atoms in some of them occupy two equivalent positions. All the metal atoms in $\{Co_{36}\}^{6-}$, which has a C_i symmetry, have a distorted octahedral coordination comprising O atoms of malonate groups, OH-groups, or water molecules. Some O atoms of the malonate groups serve as bridges between cobalt(II) ions. Formally, $\{Co_{36}\}^{6-}$ incorporates only 12 water molecules, 16 water molecules are coordinated to the K ions, while the remaining 58 ones are crystallization water molecules that are bound *via* hydrogen bonds.

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