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CRYSTAL STRUCTURE OF COBALT(II) 1,12-DODECANEDIOATE TRIHYDRATE: A NEW LAYERED COORDINATION NETWORK

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Reaction of cobalt hydroxide with the α,ω-dicarboxylic acid and 1,12-dodecanedioic acid under ambient conditions results in the formation of a trihydrate $Co(C_{12}H_{20}O_4)(H_2O)_3$ (**1**). Single crystal X-ray diffraction studies show **1** to crystallise in the orthorhombic space group *Pccn* with cell parameters $a = 40.2343(7)$ Å, $b = 8.1519(1)$ Å, $c = 9.1011(2)$ Å. The structure has a very pronounced two dimensional character, with a separation of hydrophobic *n*-alkyl chains from the carboxylate groups, the Co^{2+} cations and the water of crystallisation. The structure is discussed in respect of the structures of other known compositionally related compounds, including the dihydrate $Co(C_{12}H_{20}O_4)(H_2O)_2$.

Keywords: cobalt, layered compound, carboxylate bridge, pseudopolymorphism.

The interest in the chemical and physical properties of transition metal coordination networks (now often referred to as MOFs — metal organic frameworks) is rapidly increasing. This is because many have characteristics that make them appealing as candidate materials in areas such as gas absorption [1], gas separation [2], catalysis [3], luminescence [4], and magnetism [5, 6]. In the design of new materials there are many strategies and parameters that can be exploited. We can use ligands with well defined chelating coordination modes to produce well defined arrays of metal ions, whether they are discreet clusters [7] or infinite arrays [8]. A reduction of specificity of the coordination mode introduces some flexibility in the possible metal coordination geometries, but can still retain predictable gross structural features in the metal atom distribution. This is certainly seen with aryl carboxylate ligands such as the rigid 1,2,4,5-benzene tetracarboxylate [9]. With alkyl carboxylates we introduce a conformational flexibility to the ligand, and we also introduce the hydrophobic alkyl-alkyl interactions which when the alky chain is long enough, result in a layered 2D lamella character to a material. We describe here the structure of $Co(O_2C(CH_2)_{10}CO_2)(H_2O)_3$ (**1**) and comment on its structural relationship to a growing family of transition metal soaps.

Experimental. C and H analysis was obtained using an Exeter Analytical Inc. CE-440 Elemental Analyser. Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as pressed KBr pellets; UV-visible spectra were recorded on a Perkin Elmer Lambda 19 spectrometer in diffuse reflectance mode, using powdered $BaSO_4$ as a diluting matrix. Powder X-ray diffraction was performed using a Bruker D5000 instrument with CuK_α radiation.

Synthesis of $Co[O_2C(CH_2)_{10}CO_2](H_2O)_3$ (1). A solution of NaOH (0.033 g, 0.83 mmol) in distilled water (4 ml) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.152 g, 0.64 mmol) in distilled water (3 ml), producing a blue precipitate of $Co(OH)_2$. To this mixture, 1,12-dodecanedioic acid (0.096 g,

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Table 1

Crystallographic data and refinement parameters for **1**

Formula	$CoC_{12}H_{26}O_7$
Formula weight, $g \cdot mol^{-1}$	341.26
Crystal system	orthorhombic
Space group	*Pccn*
a, *b*, *c*, Å	40.2343(7), 8.15190(10), 9.1011(2)
V, Å^3	2985.03(9)
Z	8
ρ_{calc}, $g \cdot cm^{-3}$	1.519
Temperature, K	150
Total / Unique reflections	9706 / 2978
$\mu(MoK_\alpha)$, mm^{-1}	1.177
R_{int}	0.0418
Parameters	205
Restraints	0
$R1[F^2 > 2\sigma(F^2)]$ (all data)	0.0351 (0.0495)
$wR2[F^2 > 2\sigma(F^2)]$ (all data)	0.0830 (0.0883)
GOOF	1.039
CCDC reference number	847260

0.45 mmol) was added with stirring. The reaction was allowed to stand for one week during which time the blue precipitate changed into a pink polycrystalline product (0.140 g, 91 %). Found: C, 44.64; H, 7.41%. Calculated for $CoC_{12}H_{26}O_7$: C, 42.23; H, 7.68%. IR $\nu(cm^{-1})$ ~3400 br s and ~3300 br s (νH_2O), 2939 s, and 2920 s (νCH_2 asym), 2851 s (νCH_2 sym), 1639 s, 1618 s, 1548 br vs, 1464 s, 1414 s (νCCO_2). UV/visible λ(nm) 675 [$^4T_{1g} \rightarrow {}^4A_{2g}$], 539 [$^4T_{1g} \rightarrow {}^4T_{1g}(P)$], 485 sh.

X-ray diffraction analysis. Data was collected on a pink crystal with dimensions 0.40×0.08× ×0.01 mm^3, using an Enaf Nonius Kappa CCD area detector as ϕ and ω scans to fill the Ewald sphere. Data collection and scaling was performed with the program DENZO [10]; a semi-empirical absorption correction was applied [11]; the structure solution was achieved by direct methods (SHELXS [12]) and refined with a full-matrix least-squares on F^2 (SHELXL [13]). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the alkyl chain were fixed in ideal geometries and refined in riding mode, while the hydrogen atoms of water molecules (involved in hydrogen bonding) were located in the difference map and refined freely. Crystallographic details are given in Table 1. All crystallographic data has been deposited at the CCDC (No. 847260), from which it available free of charge on request at www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. Crystals of **1** are formed by simply mixing aqueous solutions of NaOH and $CoCl_2$, followed by the addition of the solid dicarboxylic acid. Perhaps not surprisingly the reaction is relatively slow, as both the precipitated blue $Co(OH)_2$ and the diacid have relatively low aqueous solubilities. After the mixture is left to stand for about one week the reagents are consumed and replaced by the pink microcrystalline product. The size of the crystallites and speed of this transformation is greatly affected by the relative concentrations of the reagents. For example, a slight excess of Co(II) ions results in crystals large enough for single crystal structural determination. Microanalysis and powder X-ray diffraction show that this synthetic method produces a mixture of crystals of the trihydrate $Co[O_2C(CH_2)_{10}CO_2](H_2O)_3$ (**1**) and the dihydrate [14].

The structure of **1** has a 2D character, consisting of alternating layers of the fully extended dicarboxylate ligand and layers of metal ions (Fig. 1). This is not at all surprising given the amphiphilic nature of the ligand, with a long hydrophobic alkyl section and the hydrophilic carboxylate groups at each end. This type of lamella structure is well known in the field of liquid crystals, where the addition

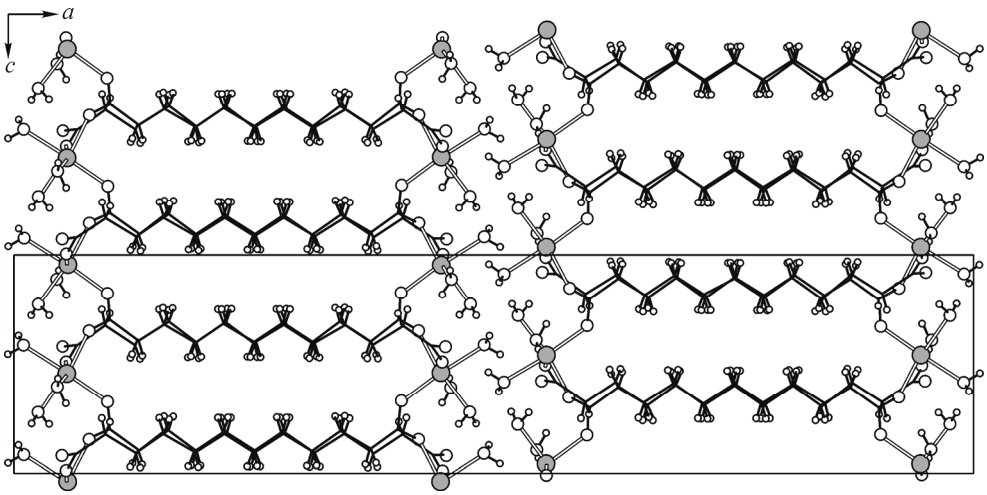

Fig. 1. View along the crystallographic *b* axis of **1**, showing the segregation of the components into hydrophobic layers containing the alkyl chains which alternate with polar layers containing the carboxylate groups, the Co(II) ions and water molecules

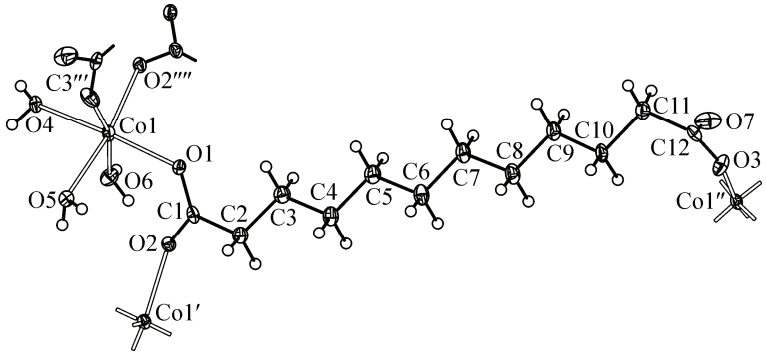

Fig. 2. Asymmetric unit and selected symmetry equivalent atoms, with thermal ellipsoids at 50 % probability.
Showing the environment of the Co(II) ion and the coordination of the ligand

of such long alkyl chains is used to stabilize smectic phases [15—17]. This layered feature is also characteristic of other metal α,ω-dicarboxylates, where the chain length is sufficiently long [18—23]. In **1** the alkyl chains pack together to form a hydrophobic layer about 12.5 Å thick. The ligand adopts the minimal energy all *trans* conformation (Fig. 2); the orientation of the out-stretched alkyl chain is tilted with respect to the layer normal. The carboxylate at C1 is slightly asymmetric with C—O bond lengths of 1.256(2) Å and 1.274(2) Å (Δ = 0.018(2) Å), while the carboxylate at C12 is effectively delocalised with C—O bond lengths of 1.255(2) Å and 1.260(2) Å (Δ = 0.005(2) Å). At the layer surface the carboxylate groups coordinate the cobalt ions. The ligand lacks crystallographic symmetry and the carboxylate groups at either end are inequivalent. The single Co(II) ion experiences a distorted octahedral coordination environment; it is bonded by three ligand molecules and three waters. The Co—O distances all lie in the range 2.053—2.165 Å. Thus one carboxylate group shows a monodentate coordination while the other coordinates in the fairly common *syn*, *anti*-1,3-bridging mode [24]. The bridging carboxylate links Co ions into a chain running along the ***c*** axis with a Co(1)—Co(1′) separation of 4.877 Å (′ = *x*, 1/2–*y*, *z*–1/2). Neighbouring chains form a ″layer″ of metal ions, with through-space Co(1)—Co(1″) distances of 5.073 Å (″ = 1–*x*, –*y*, 1–*z*). In contrast, the interlayer separation of ions is 15.76 Å. The three remaining coordination sites are all filled by water molecules, which form a complex 2D hydrogen bonded network. Hydrogen bond geometric parameters are given in Table 2.

Table 2

Geometric characteristics of H-*bond interactions in* **1**

D H A	*d*(D—H, Å	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg.
O4 H04A O3	0.78(3)	2.13(3)	2.862(2)	144(3)
O4 H04A O7	0.78(3)	2.49(3)	3.230(2)	158(3)
O4 H04B O5	0.74(3)	2.05(3)	2.755(2)	160(3)
O5 H05A O4	0.81 (3)	1.97(3)	2.776(2)	120(3)
O5 H05B O7	0.79 (3)	1.91(3)	2.678(2)	163(3)
O6 H06A O7	0.83(3)	1.91(4)	2.712(2)	162(3)
O6 H06B O2	0.78 (3)	1.93(3)	2.658(2)	156(3)

We note a bifurcated H-bond interaction between H04A and the carboxylate at C12. This type of interaction, which is given by the graph $R_1^2(4)$, is well known [25]. We also note that the water molecules O4 and O5 hydrogen bond to form a homodromic chain, which spirals along the *b* axis.

Compounds that differ in their degree of hydration are not strictly polymorphs. They are often termed pseudopolymorphs, as an indication that the structures may be related in a broader structural landscape. Changes in packing due to the change in the hydration level can result in small structural changes, such as conformational isomerism [26], alternatively a change in hydration which results in a change in the metal coordination sphere, may radically change the structure [27]. In this case, the structure of $Co(C_{12}H_{20}O_4)(H_2O)_3$ (**1**) is clearly related to the previously reported dihydrate $Co(C_{12}H_{20}O_4)(H_2O)_2$ [14]. The reduced hydration in the dihydrate results in the formation of a 1,3-chelating mode from the non-bridging end of the dioate ligand. Despite the change in metal coordination geometry, the dihydrate and trihydrate (**1**) show essentially very similar structures, with one carboxylate group linking cations into a chain structure. The comparative bridging geometries for these two structures are shown in Fig. 3. The change in local coordination at the metal is related to a change in the packing of the alkyl groups. In the dihydrate the dioate ligands are all aligned nearly parallel, and perpendicular to the layer. This is not the case in **1**, where we see alternate tilting away from the layer normal in the *b* direction by ±14.6°. We also examined the structures of other simple transition metal dioates, with chain lengths between C_6 and C_{11}. We expected some odd-even effects because of the different orientations of the carboxylate groups for an all *trans*-ligand geometry. This is clearly seen in some cases: $Co(C_9H_{14}O_4)(H_2O)_4$ [18] exists as a dimeric molecule, while $Ni(C_8H_{12}O_4)(H_2O)_4$ [19] has a 1D chain structure, in which individual carboxylate groups neither bridge nor chelate. We also expected some similarities between a compound with the same degree of hydration, where alkyl chain lengths differ by two units. This is indeed the case for the structure of **1** which is exceptionally similar to $Mn(C_{10}H_{16}O_4)(H_2O)_3$ [20]. Both compounds crystallize in the same space group, with the same packing and structural features. The only difference is the extra —CH_2CH_2— unit in **1**, making the *a* axis significantly longer. However, a further reduction in chain length, as in $Mg(C_8H_{12}O_4)(H_2O)_3$ results in an altogether different structure [21]. We note the structures of $Co(C_{12}H_{20}O_4)(H_2O)_2$ [14] and $Co(C_8H_{12}O_4)(H_2O)_2$ [22] which differ only in chain length, also have very similar arrangements of their atoms, and the greatest difference is the interlayer separation.

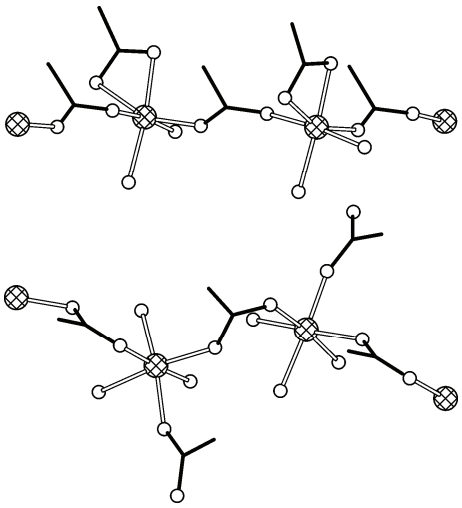

Fig. 3. Comparison of the metal environment, showing the bridging, chelating and monodentate coordination by the carboxylate ligands. *Top*: The structure in the dihydrate with an *anti-anti* 1,3-bridging carboxylate. *Bottom*: The structure in trihydrate (**1**) with an *anti-syn* 1,3-bridging carboxylate

However, $Cd(C_8H_{12}O_4)(H_2O)_2$ [23] is significantly different, with alkyl groups now making a more acute angle with the layer normal. Further reduction in alkyl chain length is accompanied by a reduction in the importance of these hydrophobic interactions, and in the related structures $M(C_6H_8O_4)(H_2O)_2$ [M = Zn, Cd] [28, 29] the alkyl groups are zigzags through the layers.

The structure of **1** has many features that may have been expected given its composition. It fits well into the broader structural landscape of related divalent α,ω-alkyl dicarboxylate compounds and we can begin to see patterns and correlations between the different compounds as a function of the degree of hydration and the length of alkyl chain.

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