Structure and Magnetism of a Polycrystalline Transition Metal Soap − $Co^{II}[OOC(CH_2)_{10}COO](H_2O)_2$

Jean-Michel Rueff,[a] Norberto Masciocchi,*[b,c] Pierre Rabu,*[a] Angelo Sironi,[b] and Antoine Skoulios[a]

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Diaquacobalt(II) *n*-dodecane-α,ω-dioate (**2**) has been synthesized by metathesis of the corresponding potassium soap **1** and has been fully characterized by chemical and spectroscopic analysis. The crystal structure of **2** has been established by X-ray powder diffraction techniques combined with electron diffraction experiments. It crystallizes in a monoclinic cell [$P2_1/a$; a = 9.6558(8), b = 7.4793(6), c = 19.8936(2) Å, β = 95.648(9)°, V = 1429.7(3) Å^3; Z = 2] and consists of stacked layers of cobalt(II) ions connected by carboxylato bridges, thus forming chains that extend along the a axis. These layers are separated by alkyl chains arranged quasi-perpendicularly to the polar sheets. Structure analysis reveals a rare *anti-anti* conformation of the Co–OCO–Co fragments, which is thought to be responsible for the weak antiferromagnetism of the Co^{II} chains. The exchange coupling constant between the magnetic centres has been estimated as J = –2.08 K.

Introduction

Low-dimensional magnetic compounds, in which the magnetic centres are arranged in well-separated, one-dimensional rows or two-dimensional layers, for instance, may be fully understood and quantitatively analysed on theoretical grounds.[1−5] Their systematic investigation is therefore expected to provide useful information on the relationship between their properties and their chemical and crystal structures, and thus to help towards the design of novel magnetic materials, hopefully with high T_C values.

In this respect, lamellar transition metal soaps[6,7] are very appealing model compounds. As shown by systematic investigations of their X-ray powder diffraction (XRPD) fingerprints,[6,8,9] it has long been known that, like micelles[10] and liquid-crystalline phases,[11−13] these materials can adopt ordered structures, although the details of these structures have been only rarely established owing to the difficulty in growing suitable single crystals.

As established previously, grafting of dicarboxylates onto parallel metal-containing layers is expected to afford highly crystalline powders, for which a complete 3D structure may be determined,[14] and to permit control over the spin coupling if suitable magnetic metal ions are employed.[15] Accordingly, the aims of the present paper are: (i) to outline the synthesis of one long-chained cobalt(II) soap, $Co^{II}[OOC(CH_2)_{10}COO](H_2O)_2$, i.e. diaquacobalt(II) *n*-dodecane-α,ω-dioate (**2**), (ii) to describe its crystal structure in detail, as elucidated by XRPD methods combining ab initio techniques (a method recently promoted by us in the field of coordination chemistry[16]) with electron diffraction analysis, and (iii) to discuss its magnetic behaviour in terms of its chemical bonding and crystal structure.

Results and Discussion

Compound **2** was prepared as a pink powder by metathesis of the corresponding potassium soap **1** with a stoichiometric amount of cobalt(II) acetate tetrahydrate, according to the precipitation method generally used in the synthesis of heavy metal soaps.[17,18] To ensure its chemical (and magnetic) purity and the coordination state of the cobalt atoms, special care was taken in choosing the operating conditions (high purity of reactants and solvents, low concentration and temperature, strict stoichiometry). The chemical nature of the product was ascertained by a set of complementary analytical techniques and was fully confirmed by XRPD.

The room-temperature diffraction pattern of **2** contains a subset of low-angle, equidistant, sharp reflections (00*l*), indicative of a lamellar structure with a spacing of ca. 19.9 Å. This value, which is larger than that determined for *n*-dodecane (17.2 Å[19]), suggests parallel, all-*trans*-alkyl chains oriented perpendicularly to the layers. Moreover, the overall complexity of the XRPD pattern is indicative of a well-developed three-dimensional crystalline arrangement. Although too intricate to be interpreted straight away in terms of a 3D crystal lattice (using conventional cell determination procedures), the pattern was eventually indexed

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[a] Institut de Physique et Chimie des Matériaux de Strasbourg,
UMR 75046 CNRS-ULP-ECPM,
23 rue du Loess, 67037 Strasbourg Cedex, France
Fax: (internat.) + 33-3/88107247
E-mail: pierre.rabu@ipcms.u-strasbg.fr
[b] Dipartimento di Chimica Strutturale e Stereochimica Inorganica e Centro CNR "CSSSCMTBSO", Università di Milano,
Via Venezian 21, 20133 Milano, Italy
[c] Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Università dell'Insubria,
Via Valleggio 11, 22100 Como, Italy
Fax: (internat.) + 39-02/7063-5288
E-mail: norberto.masciocchi@uninsubria.it

1434−1948/01/1111−2843 $ 17.50+.50/0

with the aid of additional information provided by electron-diffraction experiments. Indeed, SEM observations (Figure 1) showed that **2** apparently consists of single-crystalline platelets, thus permitting electron diffraction (ED) experiments on isolated platelets oriented perpendicularly to the electron beam. A typical ED pattern contains an extended set of sharp reflections (*hk*0; all present in the XRPD trace), consistent with a rectangular two-dimensional lattice of cell parameters $a \approx 9.6$ Å and $b \approx 7.5$ Å. Using this information, along with the knowledge of the lamellar period, the XRPD pattern of **2** was indexed on the basis of a monoclinic lattice with cell parameters $a = 9.6558(8)$ Å, $b = 7.4793(6)$ Å, $c = 19.8936(2)$ Å, and $\beta = 95.648(9)°$.[20] Systematic absences pointed to $P2_1/a$ as the probable space group, which was later confirmed by a successful crystal structure determination. Interestingly, the centred rectangular sublattice ($a' = a/2 \approx 4.8$ Å, $b' = b \approx 7.5$ Å) built-up from reflections 400, 210, 020, 420, 230, 040 of the electron-diffraction patterns (Figure 2) is identical to the two-dimensional crystal lattice that describes the lateral packing of linear paraffins in the orthorhombic form,[21] and suggests a similar packing for the alkyl chains in the crystals of soap **2**. Incidentally, the intensities of these particular reflections are especially strong, as expected from the upright orientation of the alkyl chains in the platelets.

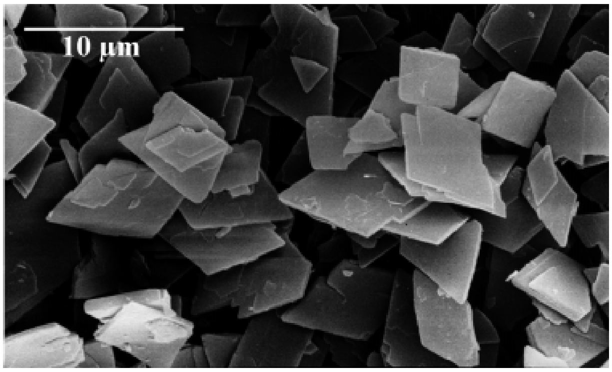


Figure 1. Morphology of powdered compound **2** as observed by scanning electron microscopy

The detailed crystal structure of **2** was established by an ab initio analysis and a Rietveld refinement of the intensity distribution in the powder X-ray diffraction patterns (see Exp. Sect.). As shown in Figure 3, the structure incorporates octahedral cobalt(II) ions *cis*-coordinated by two water molecules, as well as by one chelating [η^2-*O*,*O*] and two bridging [μ-*O*,*O*] carboxylato groups. Connected by OCO bridges in an *anti*-*anti* conformation (see Scheme 1), the Co atoms form $(-OCO-Co-)_n$ chains that extend in a zigzag fashion along *a*. Due to the glide symmetry operation, the chiral configuration of the Co atoms alternates along the chains. Arranged in slabs (with hydrophobic cores and polar surfaces), slightly tilted with respect to *c* and lying virtually perpendicular to the (*a*,*b*) planes, the fully extended dodecanedioato groups (bearing a chelating carboxylato group at one end and a bridging one at the other) connect Co atoms of opposite surfaces. These slabs are held together by hydrogen bonds between the water molecules and the carboxylic oxygen atoms, which are separated by about 2.70 Å. The separation of the Co atoms is 5.93 Å within the $(-OCO-Co-)_n$ chains, and only 5.07 Å between metal atoms of adjacent slabs (Co−O−H···O−Co).

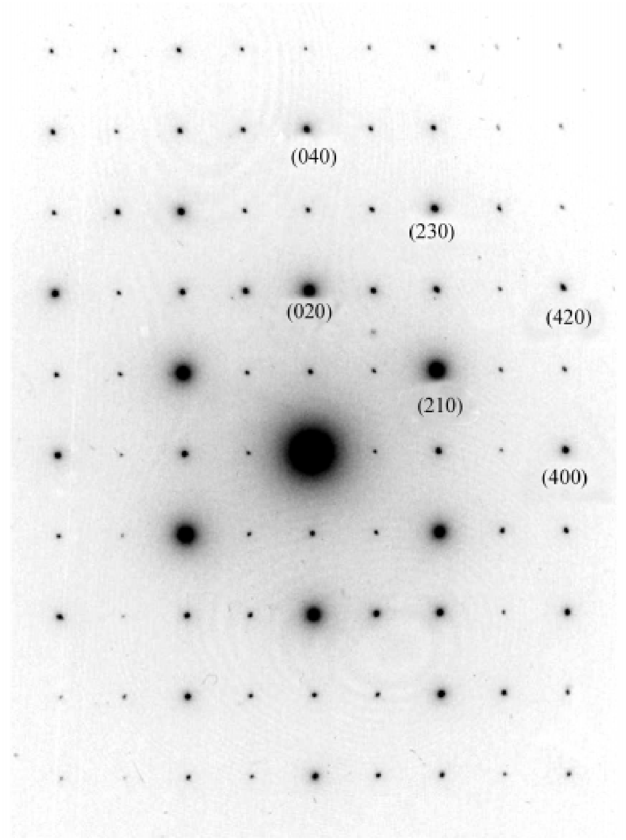


Figure 2. Electron diffraction pattern of **2** as recorded with the platelets oriented perpendicularly to the electron beam

The IR and UV data collected for **2** were readily analysed on the basis of the crystal structure. The IR spectrum features the characteristic bands of the alkyl chains in a fully stretched all-*trans* conformation. The frequency difference between the symmetric and antisymmetric carboxylate vibrations, $\Delta\nu = 128$ cm^{-1}, is smaller than that observed for the corresponding ionic potassium soap ($\Delta\nu_i \approx 150$ cm^{-1}), as befits the bidentate coordination mode of the carboxylic groups; because of the band widths, it is not possible to distinguish the chelating from the bridging mode in the structure.[22] The two broad ν(O−H) bands in the range 3200−3400 cm^{-1} can be assigned to the two hydrogen-bonded aqua ligands. The UV spectrum corroborates the quasi-regular octahedral geometry about the Co^{II} ions.[23,24] The values of *Dq* (950 cm^{-1}) and Racah's parameter *B* (846 cm^{-1}) deduced from the observed absorption bands indicate a low crystal field ($Dq/B = 1.1$), favouring the high-spin configuration observed for the metal centre (see below).

The magnetic behaviour of **2** was investigated using a SQUID magnetometer. The susceptibility χ (suitably cor-

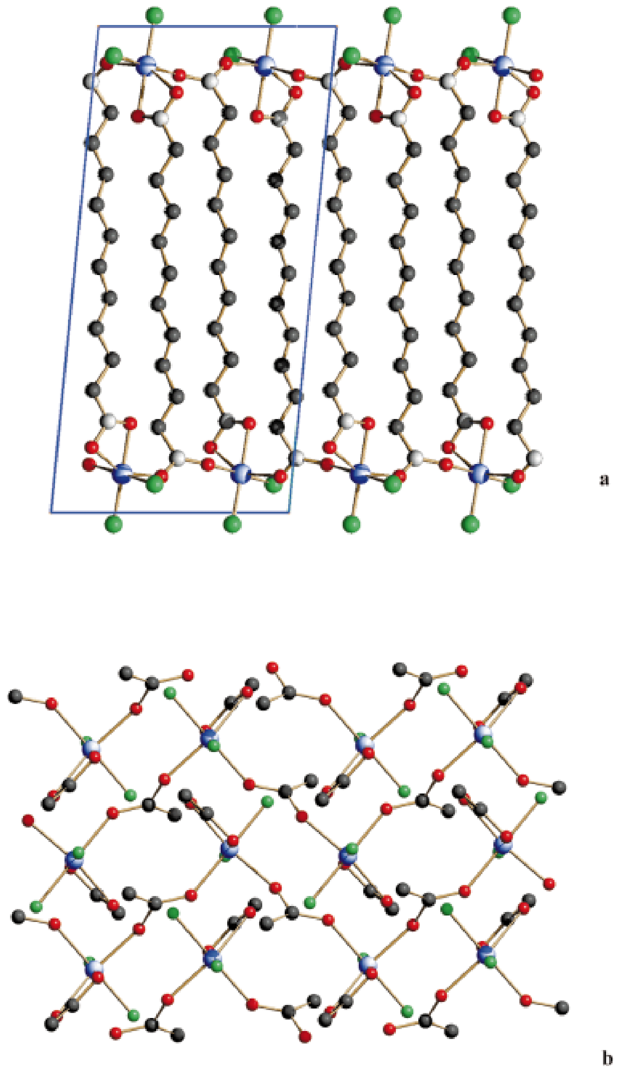
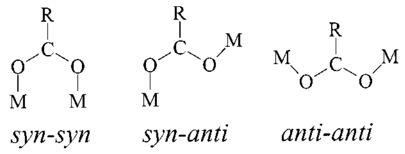


Figure 3. (a) Schematic plot (viewed down the *b* axis; horizontal axis = *a*) of the crystal structure of $Co(C_{10}H_{20}C_2O_4)(H_2O)_2$ showing the elongated organic ligands interconnecting parallel layers of octahedrally coordinated Co^{II} ions (see text); (b) a top view of the *ab* plane showing the Co^{II} chains extending along the *a* axis (horizontal) within the layers; cobalt atoms in blue; oxygen atoms of coordinated water molecules in green; for the sake of simplicity, a number of aliphatic carbon atoms have been omitted in (b)



Scheme 1

rected for sample and holder diamagnetism) grows smoothly with decreasing temperature (Figure 4), according to the Curie–Weiss law $\chi = C/(T - \theta)$ at temperatures in excess of 200 K. The value of the Curie constant, $C = 3.0$ cm^3 K mol^{-1}, is consistent with the presence of hexacoordinated high-spin Co^{II} ions ($C \approx 2.8-3.4$ cm^3 K mol^{-1})[25] and the negative sign of the Weiss temperature, $\theta = -19.7$ K, points, phenomenologically, to the existence of antiferromagnetic exchange interactions (also supported by the decrease of χT from 2.76 cm^3 K mol^{-1} at 295 K to 1.08 cm^3 K mol^{-1} at 2 K). The effect of spin-orbit coupling, known to be operative for Co^{II} ions,[5,25,26] most certainly also contributes to the decay of χT upon cooling; however, on no account does it explain entirely the observed decay. Firstly, the temperature dependence of the effective magnetic moment deduced from the experimental data differs from that calculated for isolated Co^{II} ions[26] (Figure 4); in particular, the χT value measured at 2 K (1.08 cm^3 K mol^{-1}) is significantly smaller than expected (1.8 cm^3 K mol^{-1}) for isolated Co^{II} magnetic centres. Secondly, the magnetization curve $M(H)$, saturating at $M_S = 2.2$ $\mu_B$mol^{-1} as expected (2–3 $\mu_B$mol^{-1}),[5,25] is significantly lower than that predicted by Brillouin's law[25] (Figure 5).

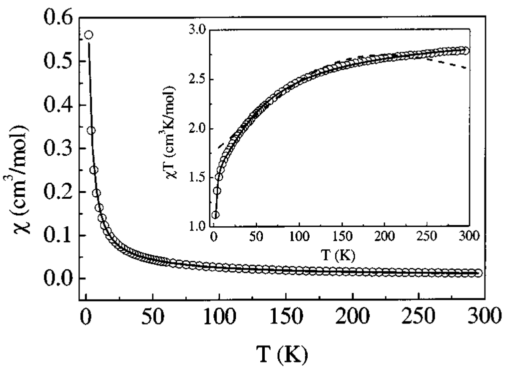


Figure 4. Temperature variation of the magnetic susceptibility of compound **2**; inset: χT vs. T variation; full lines correspond to the best fit of the experimental data with the relationship given in the text; the dashed line in the inset corresponds to the variation of $\mu_{eff}^2/8 = \chi T$ calculated from the expression given in ref.[26] for the effective moment of isolated Co^{II} ions in a weak octahedral field

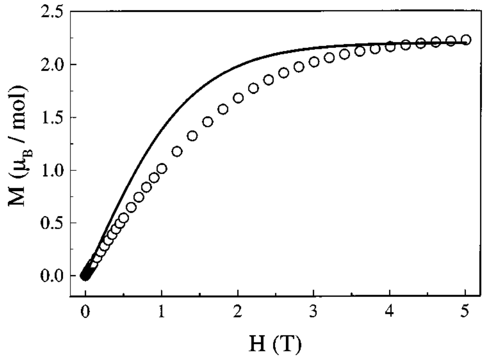


Figure 5. Magnetization vs. field curve at 2 K for compound **2**; the full line corresponds to the best fit to Brillouin's function

However weak, the antiferromagnetic coupling suggested by the experimental data most likely occurs through the carboxylato bridges along the $(-OCO-Co-)_n$ chains; although shorter, the exchange pathway through the hydrogen bonds appears to be less effective. No analytical expression is available in the literature to describe the temperature dependence of χT for chains of Co^{II} ions with spin-orbit coupling. Considering, however, that below 30 K the Co^{II}

ions generally behave as anisotropic $S = 1/2$ pseudo spins,[5,25,26] one may attempt to calculate the susceptibility by using the relationship given for Ising chains:[5,25]

$$\chi = 1/3(\chi_z + 2\chi_x)$$

with

$$\chi_z = \frac{Ng_z^2\mu_B^2}{4kT}\exp(J/2kT)$$

and

$$\chi_x = \frac{Ng_x^2\mu_B^2}{2J}\left[\tanh(J/2kT) + (J/4kT)\sec h^2(J/4kT)\right]$$

In the present case, this model turned out to be unsatisfactory as the antiferromagnetic exchange interaction is too weak to show up clearly against the spin-orbit coupling (see below) and, ultimately, because the anisotropy of the ion *g* tensor is too small.[5]

Nevertheless, in order to obtain an estimate of the strength of the antiferromagnetic exchange interaction, one may use the following simple phenomenological equation:[27]

$$\chi T = A\exp(-E_1/kT) + B\exp(-E_2/kT)$$

Here, $A + B$ equals the Curie constant, and E_1, E_2 represent the "activation energies" corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction. This equation adequately describes the spin-orbit coupling, which results in a splitting between discrete levels, and the exponential low-temperature divergence of the susceptibility [$\chi T \propto \exp(\alpha J/2kT)$]. Moreover, it is in excellent agreement with the experimental data obtained in the present work (Figure 4). The obtained values of $A + B = 3.0$ cm^3 K mol^{-1} and $E_1/k = +56.6$ K (using a least-squares fitting method) are consistent with those given in the literature for the Curie constant ($C \approx 2.8-3.4$ cm^3 K mol^{-1}) and for the effect of spin-orbit coupling and site distortion (E_1/k of the order of +100 K).[25] As for the value found for the antiferromagnetic exchange interaction, it is very weak indeed ($-E_2/k = -1.03$ K), corresponding to $J = -2.06$ K according to the Ising chain approximation [see above; $\chi T \propto \exp(+J/2kT)$].

Although rare, several examples of one-dimensional systems of transition metal(II) ions have been reported in the literature,[28−32] in which the exchange effectively occurs through carboxylato bridges of various geometries (see Scheme 1). In Cu^{II} complexes, for instance, the exchange coupling is strongly antiferromagnetic with a *syn-syn* conformation,[33] very weakly so (eventually ferromagnetic[34]) with a *syn-anti* conformation,[35−37] and weak to moderately antiferromagnetic with an *anti-anti* conformation.[38] In the present work, the *anti-anti* geometry of the diaquacobalt(II) dicarboxylate appears to favour very weak antiferromagnetic interactions.

Conclusions

The cobalt compound investigated in the present work is, to the best of our knowledge, the first example of a carboxylate-bridged chain complex of Co^{II} featuring an uncommon *anti-anti* conformation to have been fully characterized both magnetically and structurally. Indeed, this *rare* coordination mode of the μ-RCOO group was only discovered thanks to XRPD, which has allowed the determination of the complete 3D structure of a transition metal soap for the first time.[39−41] The XRPD method that we used combined the power of ab initio techniques with that of selected area electron diffraction. Such coupling of complementary techniques, eventually assisted by further computational modelling,[42−44] is expected to allow the solution of more complex crystal structures in the near future, leading to the extensive use of these methods in materials science.[27,45,46] Furthermore, the magnetic properties of **2** have been analysed in detail on the basis of its crystal structure. The weak antiferromagnetism of the carboxylato-bridged Co^{II} chains (with a *cis* coordination mode of the cobalt atoms) is attributed to an *anti-anti* configuration of the bridges.

Experimental Section

General Remarks: Thermogravimetric experiments were performed using a Setaram TG92 instrument (heating rate 2 °C/min; air stream). − Mass-spectrometric measurements were performed using a Micro Mass Trio 2000 instrument (degassing of quartz crucible at 100 °C, desolvation of soap at 200 °C). − Scanning electron microscopy was performed using a JEOL JSM-840 instrument coupled with a KEVEX energy dispersion spectrometer. − Electron diffraction experiments were performed with a Philips CM12 transmission instrument equipped with a PW6594 goniometer (120 kV). − FT-IR studies were performed with an ATI Mattson Genesis computer-driven instrument (0.1 mm thick powder samples in KBr). − UV/Vis/NIR studies were performed with a Perkin−Elmer Lambda 19 instrument (spectra recorded by reflection with a resolution of 4 nm and a sampling rate of 480 nm/min). − Magnetic studies were carried out using a Quantum Design XMPMS SQUID magnetometer. Susceptibilities were measured at 0.2 T in the temperature range 1.7−295 K. The magnetization curve was determined at 2 K with an applied field ranging from 0 to 5 T. − For the powder X-ray diffraction experiments, the powder samples were cautiously deposited in the hollow of a side-loaded holder. Data were collected with a Siemens D500 diffractometer equipped with Soller slits, a primary-beam curved quartz monochromator (Co-$K_{\alpha 1}$, $\lambda = 1.78897$ Å), an Na(Tl)I scintillation detector, and a pulse height amplifier discriminator. The generator was operated at 35 kV and 30 mA. Slits used: divergence 1.0°, antiscatter 1.0°, and receiving 0.15 mm. Long overnight scans were performed in the range $2° < 2\theta < 130°$ with a θ/2θ step-scanning mode ($\Delta 2\theta = 0.02°$ and $t = 10$ s). The indexing procedure is described in the text.

Potassium *n*-Dodecane-α,ω-dioate, $C_{12}H_{20}K_2O_4$ (1): A 0.1 N aqueous solution of KOH (5.611 g, 0.1 mol; Titrisol, Fluka) was diluted with acetone (150 mL; Carlo Erba, analytical grade) and added dropwise to a stirred solution of *n*-dodecane-α,ω-dioic acid (11.515 g, 0.05 mol; Lancaster, 99%) in acetone (500 mL) and the mixture was refluxed for 3 h (56.5 °C). After cooling to room temperature, a white precipitate of the potassium soap had formed, which was collected by filtration, washed repeatedly with hot acetone, and dried in vacuo at room temperature for 12 h.

Diaquacobalt(II) *n*-Dodecane-α,ω-dioate, $C_{12}CoH_{24}O_6$ (2): Pure **1** (1.96 g, 6.4 mmol) was dissolved in a mixture of demineralized water (18.2 MΩcm; Millipore) and ethanol (purum; Carlo Erba) (300 mL, 1:1, v/v). The resulting solution was added dropwise to a stirred solution of $(CH_3COO)_2Co{\cdot}4H_2O$ (1.59 g, 6.4 mmol; Aldrich, 99.999%) in demineralized water (40 mL) at 20 °C. After stirring for 3 h, a pink precipitate of the diaquacobalt dicarboxylate had formed, which was collected by filtration, washed repeatedly with aqueous ethanol (1:1, v/v), and dried in vacuo at room temperature for 24 h (yield 82%). The presence of water molecules was detected by thermogravimetry (TGA) (10.8% weight loss at about 90 °C) and confirmed by mass spectrometry. The purity of the product was confirmed by elemental analysis (EA) {$Co[OOC(CH_2)_{10}COO](H_2O)_2$: calcd. C 44.6, H 7.5; found C 44.3, H 7.5}, oxidative pyrolysis (OP) (heating in air from 20 to 700 °C at 2 °C/min, maintaining at 700 °C for 30 min to transform cobalt into Co_3O_4,[47,48] and cooling to 20 °C at 10 °C/min: calcd. Co 18.2; found 18.4), and Karl Fischer (KF) titration of water (calcd. 11.2; found 12.5) (water molecules per Co atom: 1.9 by TGA, 2.2 by KF, 1.9 by OP, and 2.1 by EA). − IR (KBr pellet): $\tilde{\nu}$ = 3401 [ν(OH−O)], 3262 [ν(OH−O)], 1670 [$\delta_b(H_2O)$], 2919 [$\nu_{as}(CH_2)$], 2850 [$\nu_s(CH_2)$], 1542 [$\nu_{as}(C{=}O)$], 1470 [$\delta_s(CH_2)$], 1414 [$\nu_s(C{-}O)$], 723 cm^{-1} [$\rho(CH_2)$]. − UV/Vis (reflectance for octahedral coordination of Co^{II}): λ = 1316 nm ($^4T_{1g} \rightarrow {}^4T_{2g}$), 714 nm ($^4T_{1g} \rightarrow {}^4A_{2g}$), 543 nm [$^4T_{1g} \rightarrow {}^4T_{1g}(P)$].

X-ray Crystallographic Study: The structure solution of **2** was initiated using EXPO,[49,50] which revealed the positions of the cobalt atom and of a few oxygen atoms bound to it. With the help of difference Fourier syntheses and geometrical modelling, approximate coordinates for *all* the remaining non-hydrogen atoms were subsequently obtained. All refinements were performed with the aid of the GSAS suite of programs,[51] by imposing steric restraints on the organic fragments, which were idealized with average literature values (C−C 1.54 Å; C−C−C 109.5°). Soft restraints were also applied to Co−O distances and C−O interactions in order to maintain plausible Co−O−C and O−C−O angles. The peak shapes were best described by the Thompson/Cox/Hastings formulation[52] of the pseudo Voigt function, with GV and LY set to zero. The experimental background was modelled by a cosine Fourier series, while systematic errors were corrected with the aid of sample-displacement angular shifts and preferred orientation corrections [with (001) pole]. Metal atoms were given a refinable isotropic displacement parameter of $U_{iso}(M) = 0.028(2)$ Å^2, while the U values of lighter atoms were arbitrarily given values of $U_{iso}(M) + 0.02$ Å^2. The contribution of the hydrogen atoms to the scattered intensity was neglected. Scattering factors, corrected for real and imaginary anomalous dispersion terms, were taken from the GSAS internal library. The final Rietveld refinement plot is shown in Figure 6. Crystal Data: $C_{12}H_{24}CoO_6$, M_r = 323.25 g mol^{-1}, monoclinic, $P2_1/a$; a = 9.6558(8), b = 7.4793(6), c = 19.8936(2) Å, β = 95.648(9)°, V = 1429.7(3) Å^3; Z = 2; μ = 100.48 cm^{-1}; ρ = 1.502 g cm^{-3}. The final R_p, R_{wp}, and R_F agreement factors, for 6001 data collected in the 4−124° range (1442 reflections), were 0.125, 0.163, and 0.067, respectively. Full pattern decomposition resulted in R_p and R_{wp} values of 0.108 and 0.146, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156267. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

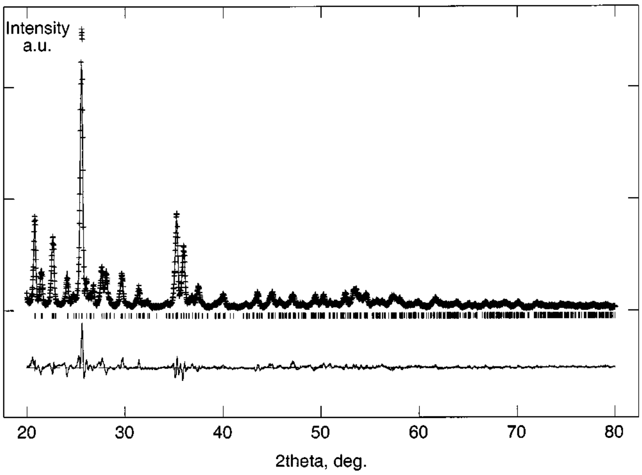


Figure 6. Rietveld refinement plot of compound **2** in the 20−80° (2θ) range, with difference plot and peak markers at the bottom; the low-angle section, dominated by the strong (001) peak, has been omitted in order to highlight the agreement at intermediate angles

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