Synthesis, Structure and Magnetic Properties of the Cobalt(II) 1,1′-Biphenyl-2,2′-dicarboxylate Hydroxide Chain Compound $[Co_3\{O_2CC_{12}H_8CO_2\}_{2.5}(OH)(H_2O)_2]_n$

Jean-Michel Rueff,[a] Sébastien Pillet,[b] Gautier Bonaventure,[a] Mohamed Souhassou,[b] and Pierre Rabu*[a]

Keywords: Carboxylate ligands / Hydrothermal synthesis / Cobalt / Magnetic properties

A new 1D compound $[Co_3(O_2CC_{12}H_8CO_2)_{2.5}(OH)(H_2O)_2]$ (**2**) was synthesised with the hydrothermal method from $Co(NO_3)_2$·$6H_2O$, 1,1′-biphenyl-2,2′-dicarboxylic acid, and KOH under hydrothermal conditions. Its structure was solved by single-crystal X-ray diffraction analysis. Compound **2** crystallises as purple crystals with the monoclinic cell (*C*2/*c*) *a* = 19.370(1), *b* = 14.5350(9), *c* = 22.583(1) Å, β = 89.910(4)°. The structure consists of chains of butterfly motifs of Co^{II} ions in both octahedral and tetrahedral oxygen sites. The structural, IR and UV spectroscopic data and magnetic behaviour are presented and compared to that of the parent pink compound **1**, obtained under slightly different stoichiometric conditions. Ligand-field characteristics, $Dq \approx 1146$ cm^{-1} and $B \approx 811$ cm^{-1} for the octahedral sites, and $Dq \approx 434$ cm^{-1} and $B \approx 782$ cm^{-1} for Co^{II} in the tetrahedral sites, were deduced from the electronic spectra and related to the structural and magnetic findings. From the magnetic point of view, the occurrence of efficient Co–O–Co superexchange pathways contributes to significant antiferromagnetic coupling between the cobalt(II) ions along the chains.

Introduction

The design and construction of new polymeric compounds of tuneable dimensionality, through adapted synthetic routes, is of strong interest in materials chemistry.[1] In particular, the solvothermal or hydrothermal route is currently being developed in solid-state and coordination chemistry,[2,3] for the design of new architectures, such as layered compounds,[4,5] helical chain polymers,[6–9] organic-inorganic compounds,[10–12] or mesoporous materials.[13–15] In this method, the organic ligand acts as a template, the structure of the product being closely related to the geometry and the number of coordination sites provided by the ligand. It has also been shown that solvothermal conditions are quite versatile, slight variations in temperature, reaction time, concentration or molar ratio between reactants may lead to very different products.[13] Nowadays these techniques are applied in the design of new low-dimensional (1D, 2D) magnetic compounds, whose study is particularly useful for a better understanding of the mechanisms responsible for magnetic coupling in solids.[16–19] Indeed, correlations between the magnetic properties of molecule-based solids and their structure, or the nature of the chemical bond between magnetic centres is largely used for the design of new magnetic materials, including high T_C magnets.[20–23] For the synthesis of new coordination compounds with extended structures, the use of dicarboxylate ligands provides many examples where magnetic transition-metal ions are arranged within various kinds of networks. The structural variety of these compounds arises from the carboxylate ligand, which is able to adopt different coordination modes, exhibiting either unidentate or chelating or bridging bidentate modes.

In a previous study[24] we reported on the structural and magnetic properties of two isostructural 1D polymers, obtained from the reaction of 1,1′-biphenyl-2,2′-dicarboxylic acid (diphenic acid) with KOH and $Co(NO_3)_2$·$6H_2O$ and $Ni(NO_3)_2$·$6H_2O$ under hydrothermal conditions. Their structure consists in the stacking of helical chains of M^{II} ions in octahedral coordination. In the case of the Co^{II} analogue, $[Co_2(O_2CC_{12}H_8CO_2)_2(H_2O)_8]$ (**1**), another phase was observed, depending on the synthesis conditions, and appearing as purple needle-shaped crystals. After slightly varying the synthesis conditions, we were able to isolate this purple phase and this paper describes its crystal structure and magnetic properties. A comparison is also made with the previous pink compound **1**.

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[a] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 75040 du CNRS,
23 rue du Loess, 67034 Strasbourg, France
Fax: (internat.) + 33-3/88107247
E-mail: Pierre.rabu@ipcms.u-strasbg.fr
[b] Laboratoire de crystallographie et modélisation des matériaux minéraux et biologiques, Faculté des Sciences, UHP,
B. P. 239, 54506 Vandoeuvre-les-Nancy Cedex

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Results and Discussion

Structural Results

$C_{35}H_{25}Co_3O_{13}$ crystallises in the monoclinic *C2/c* space group with *a* = 19.370(1), *b* = 14.5350(9), *c* = 22.583(1) Å, β = 89.910(4)°. Selected bond lengths and angles are summarised in Table 1. The asymmetric unit (see Figure 1) consists of four non-equivalent cobalt atoms of octahedral and tetrahedral coordination, 2.5 biphenyl dicarboxylate ligands, one hydroxy ion and two water molecules. Moreover, two of the cobalt atoms are located on symmetry elements: Co2 on a centre of symmetry and Co4 on a twofold axis. Three Co atoms (Co1, Co2 and Co3) are located in octahedral environments CoO_6, whereas Co4 lies in a quasi-perfect tetrahedral oxygen surrounding (see Figure 2). The hydroxy ion, the water molecules and the two carboxylate groups of each biphenyl dicarboxylate ligand are involved in the Co coordination.

Table 1. Selected bond lengths (Å) and angles (°) for compound **2**

Co1−O1	2.178(4)	Co3−O2	2.047(3)
Co1−O2	2.046(3)	Co3−O12	2.074(4)
Co1−O3	2.329(4)	Co3−O11	2.078(4)
Co1−O4	2.067(3)	Co3−O7	2.111(4)
Co1−O5	2.142(3)	Co3−O8	2.143(5)
Co1−O6	2.037(3)	Co3−O9	2.134(4)
Co2−O2	2.068(3)	Co4−O5	1.959(3)
Co2−O1	2.222(3)	Co4−O10	1.922(4)
Co2−O7	2.124(3)		
C1−O6	1.258(6)	C8−O12	1.250(6)
C1−O11	1.250(6)	C20−O3	1.244(6)
C2−O13	1.235(6)	C20−O5	1.304(6)
C2−O7	1.296(6)	C27−O4	1.263(6)
C8−O1	1.286(6)	C27−O10	1.266(6)
Co1···Co2	3.2883(7)	Co1···Co4	3.2028(8)
Co1···Co3	3.4370(9)	Co2···Co3	3.1416(7)
O9(H20)···O11	2.704(5)	O9(H24)···O13	2.686(6)
O8(H17)···O12	3.065(6)	O8(H25)···O9	3.240(6)
Co1−O1−Co2	96.70(14)	Co3−O2−Co2	99.50(13)
Co1−O2−Co3	114.24(15)	Co4−O5−Co1	102.62(16)
Co1−O2−Co2	106.11(16)	Co2−O7−Co3	95.75(13)
O9−H20−O11	114(4)	O9−H24−O13	174(5)
O8−H17−O12	118(3)	O8−H25−O9	127(4)

The C−O bond lengths in the five carboxylate fragments of the asymmetric unit range from 1.235(6) Å to 1.304(6) Å. This dispersion reflects the weakening of the C−O bonds due to the Co···O interactions. The only oxygen atom, O13, which is not coordinated to a cobalt atom presents the shortest C−O bond [1.235(6) Å], whereas the longest bond lengths, 1.286(6) Å, 1.304(6) Å and 1.296(6) Å, correspond to O1, O5 and O7, respectively, which are all involved in the coordination polyhedron of two Co atoms. The mean C−O bond length for oxygen atoms coordinated to only one cobalt atom is 1.258(10) Å.

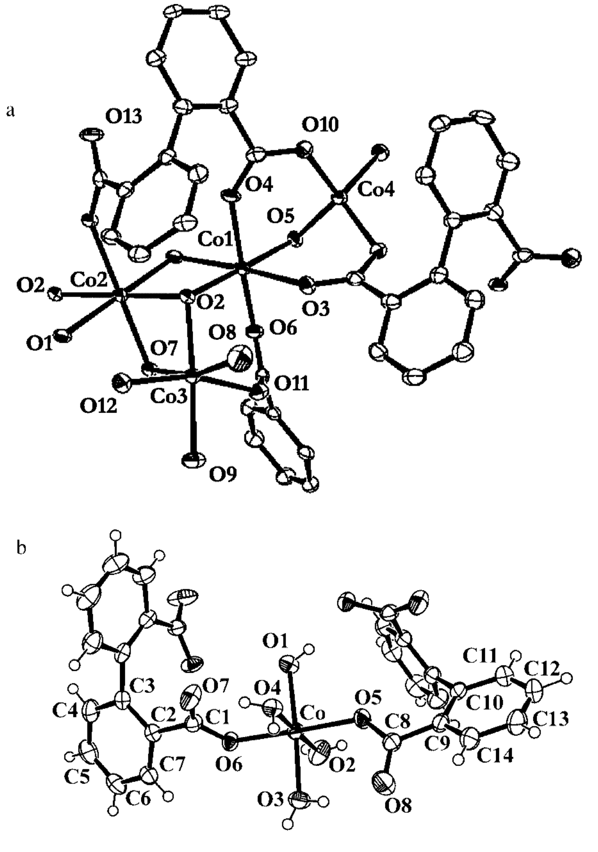


Figure 1. ORTEP drawing of the asymmetric unit of a) compound **2** $Co_3C_{35}O_{13}H_{25}$ and b) for compound **1**, with the atom labelling (some equivalent O atoms have been generated to complete the Co coordination, H atoms omitted; the ellipsoids are plotted at 50% level)

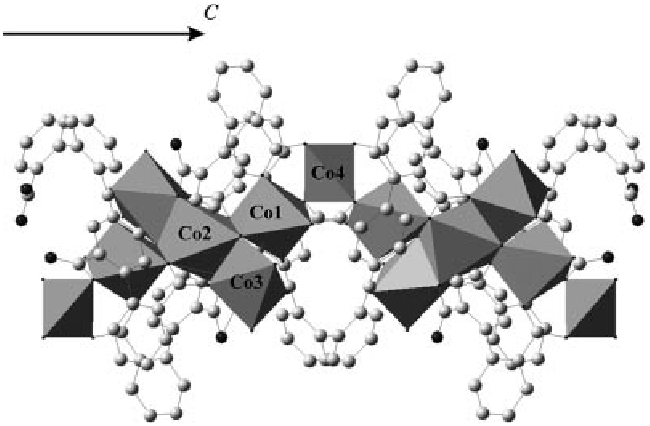


Figure 2. Octahedra and tetrahedron connectivity along one chain in compound **2**

Two oxygen octahedra (around Co1 in position *8f* and Co2 in *4a*) and the tetrahedron (around Co4 in *4e*) are connected through chains along the crystallographic *c* axis (see Figure 2) as a repetition of the symmetry block ··Co4···Co1···Co2···Co1···Co4···. The last octahedron around Co3 in the *8f* position is located on the side of the chain. The Co−Co distances range from 3.1416(7) Å to 3.4370(9) Å for Co2−Co3 and Co1−Co3, respectively. Contrary to the tetrahedron, the octahedral sites are far from being regular. As shown by the dispersion in bond lengths given in Table 2, the Co−O bond lengths range from 2.037(3) Å to 2.329(4) Å for the octahedra, while the metal-oxygen distances for the tetrahedron are 1.922(4) Å and 1.959(3) Å. The particular geometry exhibited by the chain thus implies four specific exchange pathways, with different characteristics (see Table 2). Co1 and Co2 are connected through one oxygen atom from a hydroxy group (O2) and one oxygen from a carboxylate group. The Co2−Co3 pathway involves an identical geometric configuration. The Co1 and Co3 atoms are connected by a hydroxy ion (O2) and through an O−C−O bridge of a carboxylate group. Finally, one oxygen atom from a carboxylate group (O5) and two O−C−O pathways are involved in the Co1−Co4 connection. Based only on these geometric considerations, one can expect a rather complex situation for the Co-Co magnetic interactions along the chain.

As shown in Figure 3, no contact, and especially no hydrogen bonds, are observed between the chains, the phenyl rings of the biphenyl dicarboxylate ligands being located away from the chain axis. The two water molecules are nevertheless involved in four intra-chain hydrogen bonds whose geometrical characteristics are given in Table 1.

Interestingly, the formerly characterised compound **1**, whose structure is shown in Figure 1b, exhibits a helical arrangement of the dicarboxylate ligands. The $\mathrm{Co^{II}}$ atoms are interconnected through carboxylate bridges and surrounded by four water molecules. The Co-Co distance along the chains is 4.9981(3) Å.[24] By comparison, the present structure thus corresponds to the condensation of the $\mathrm{Co^{II}}$ chains resulting in shorter contacts between magnetic centres and in the occurrence of more efficient metal-oxygen-metal exchange pathways. Another difference is the occurrence of tetrahedral coordination for Co4.

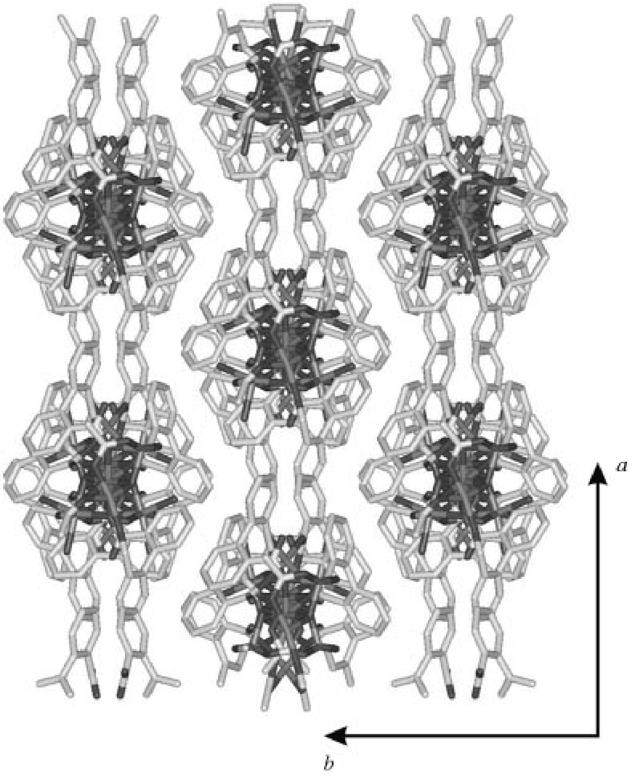
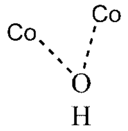
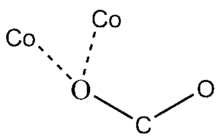
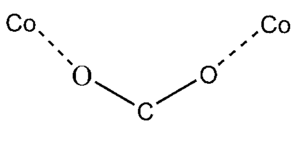


Figure 3. Crystal structure viewed along the chains in the crystallographic *c* direction for compound **2**

Spectroscopic Properties

The IR spectrum of compound **2** shows the characteristic bands of the 1,1′-biphenyl-2,2′-dicarboxylate. The fre-

Table 2. Geometric details of the different Co···Co exchange pathways in compound **2**

Co···Co connection	Co1···Co2 [3.2883(7) Å]	Co1···Co3 [3.4370(9) Å]	Co1···Co4 [3.2028(8) Å]	Co2···Co3 [3.1416(7) Å]
	X	X		X
	X		X	X
		X	X X	

quency difference between the symmetrical and antisymmetrical carboxylate vibrations, $\Delta\nu = 135\ \mathrm{cm}^{-1}$, is in agreement with the bridging bidentate coordination mode of the carboxylate groups found in the structure.[25–27] The experimental spectra do not allow to distinguish a doublet corresponding to the minority unidentate mode of one of the carboxylate functions. The presence of broad ν_{O-H} bands at 3429 cm^{-1} is related to the hydrogen-bonded aqua ligands. UV/Vis spectra (reflectance) shown in Figure 4 are consistent with the presence of both octahedral coordination {λ = 1090 nm ($^4T_{1g} \rightarrow {}^4T_{2g}$), 525 nm, [$^4T_{1g} \rightarrow {}^4T_{1g}(P)$]}, and tetrahedral coordination of Co^{II} {λ = 1280 nm [$^4A_2 \rightarrow {}^4T_1(P)$], 590 nm [$^4A_2 \rightarrow {}^4T_1(F)$]}.[28,29] The comparison with the spectrum of compound **1** (see Figure 4) indicates a different octahedral geometry for the Co^{II} ions in compound **2**, where the octahedra are found to be significantly distorted. The corresponding values of Dq ($\approx$ 1146 cm^{-1} for **2**) and Racah's parameter B ($\approx$811 cm^{-1}), deduced from the transitions assigned to the octahedral sites, agree with a low octahedral crystal field (Dq/B = 1.4) and high-spin configuration for the metal centres, also inferred from the magnetic findings (see below). The other set of transitions gives $Dq \approx 434\ \mathrm{cm}^{-1}$ and $B \approx 782\ \mathrm{cm}^{-1}$ in agreement with the presence of Co^{II} in a tetrahedral site.[28,29]

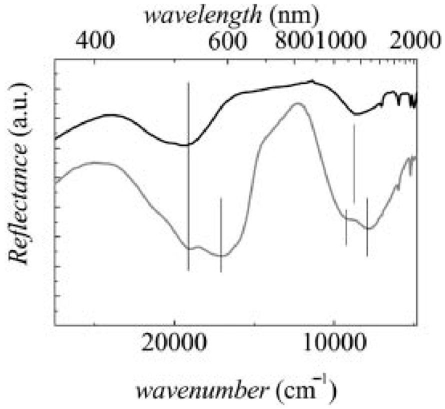


Figure 4. Reflectance UV spectra of compounds **1** (above) and **2** (below); vertical lines are guides for the eyes

Magnetic Properties

The magnetic properties of compound **2** were investigated as described in the Exp. Sect. The temperature variation of the magnetic susceptibilities, χ, is shown in Figure 5. Upon cooling down, $\chi = f(T)$ increases continuously up to a maximum of 1.9 emu·mol^{-1} at 2 K. The χT product exhibits a regular decrease from 8.35 emu·K·mol^{-1} at 300 K without tending to zero but to 2.46 emu·K·mol^{-1} at 2 K. The inverse susceptibility (not shown) varies linearly with the temperature in the high temperature regime ($T >$ 180 K) and is well fitted in this region by using the Curie–Weiss law, giving C = 8.96 emu·K·mol^{-1} and θ = −18.6 K. The Curie constant deduced for three metal ions per formula unit agrees with that expected for 5/6 octahedral high spin and 1/6 tetrahedral Co^{II} ions[30,31] with C_{octa} = 3.21 emu·K per Co^{II} mol and C_{tetra} = 1.875 emu·K per Co^{II} mol.

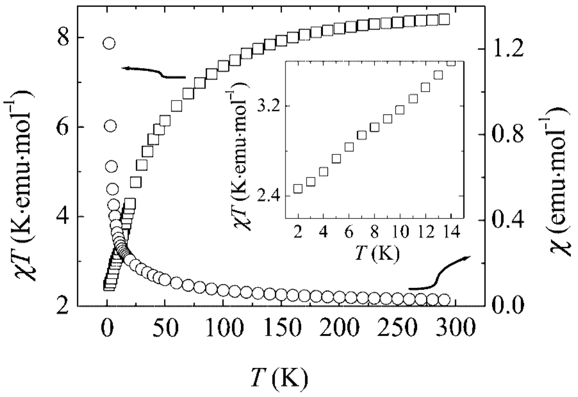


Figure 5. Temperature variation of the magnetic susceptibility (scaled to 1 formula unit) for compound **2**

The decrease of the χT product together with the negative value of θ might be related to the effect of the spin-orbit coupling for isolated Co^{II} ions in the octahedral crystal field. This results in the splitting of the energy levels arising from the $^4T_{1g}$ ground term, stabilizing the $J = \pm 1/2$ doublet well separated from the excited states.[30] However, the χT value of 2.46 emu·K·mol^{-1} at 2 K is much smaller than the minimum value expected for isolated high-spin octahedral and tetrahedral cobalt(II) centres [ca. 3 × (5/6 × 1.8 + 1/6 × 1.875) = 5.44 K.emu·mol^{-1}],[30] which suggests the occurrence of an antiferromagnetic coupling between the Co^{II} ions. It is also inferred by the magnetisation vs. field curve at 2 K (see Figure 6) that exhibits a very small "saturation" moment, Ms = 3.3 μ_B.mol^{-1} for three Co^{II} ions (expected: 2–3 μ_B per cobalt)[30,31] with a slight increase toward the high fields. However, no long-range magnetic order occurs down to 2 K.

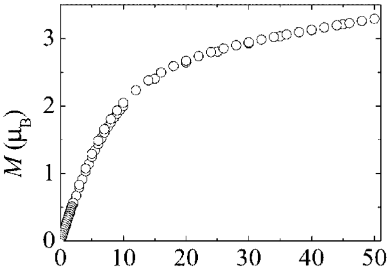
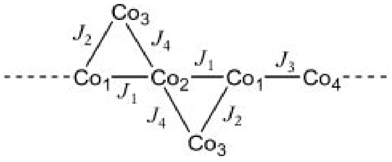


Figure 6. Magnetisation versus field variation at 2 K for compound **2** (scaled to 1 formula unit)

Magnetostructural Relationship

As summarised in Scheme 1, compound **2** can be viewed as chains formed by butterfly motifs of five octahedral Co^{II} centres interconnected through tetrahedral Co4. We identified four different exchange pathways, connecting the cobalt atoms along the chains (see Table 2), corresponding to four magnetic coupling constants: J_1, J_2, J_3 and J_4, each of which corresponds to double or triple bridges between the magnetic centres (see above). Exchange between the Co^{II} ions through the carboxylate bridge is expected to be small and antiferromagnetic.[32,33] All exchange pathways involve at least one Co−O−Co bridge that can lead either to antiferromagnetic or ferromagnetic coupling, as found in hydroxide[14,34−37] or carboxylate[38,39] compounds. The situation is thus rather complex and no analytical expression is available for computing the magnetic behaviour of Co^{II} chains by taking the spin-orbit coupling for the magnetic centres in an octahedral site into account. Also the numerical approach is limited here because of the size of the elemental unit involving six Co^{II} atoms, except for the low temperature region ($T < 30$ K), where the effect of octahedral crystal field and spin-orbit coupling results in a doublet ground-state (effective $S = 1/2$ spin). However, the system appears largely over-parameterized and attempts to fit the susceptibility data in a limited low temperature range, where no anomaly occurs, would be meaningless. What is expected is that J_2 and J_3, which correspond to an exchange through corners of neighbouring coordination polyhedra, are less efficient than J_1 and J_4, which occur through the octahedron's edges. In addition, the Co1−Co2 distance is large (3.437 Å, see Table 2) and J_2 should be negligible compared to J_1 and J_4. In this scheme, and assuming that all the interactions along the chains are antiferromagnetic (the effect of J_2 is neglected), it is worth noticing that an antiferromagnetic arrangement between neighbouring Co^{II} ions would stabilize two resulting moments within the six-centre unit, that is, the moment of one Co^{II} ion per formula unit at low temperature This fits well with the value of ca 3 μ_B observed in the magnetisation versus field curve at 2 K.



Scheme 1

Finally, compared to compound **1**, which was found to be quasi paramagnetic, the present compound, **2**, corresponds to a condensation of the structure along the chains with occurrence of efficient Co−O−Co exchange pathways. This leads to a significant antiferromagnetic interaction between neighbouring Co^{II} ions in the present compound.

Conclusion

A new one-dimensional cobalt(II) 1,1′-biphenyl-2,2′-dicarboxylate was synthesised by the hydrothermal method. The structure was solved on single crystals and consists of decorated chains of Co^{II} ions in octahedral and tetrahedral sites. Compound **2** was obtained by slightly varying the reaction conditions with respect to the previous derivative **1**, thus showing the versatility of the simple 1,1′-biphenyl-2,2′-dicarboxylate bridging ligand towards synthesis conditions. The two compounds can be considered as the result of two competing driving forces, namely templating by the ligand that stabilizes the helical chains in **1**, on the one hand, and templating through the metal coordination that leads to a more compact interconnection of the metal ions in **2**, on the other hand. The IR and UV/Vis data of the two compounds were compared and ligand field characteristics were deduced from the electronic spectra and related to the structural findings. From the magnetic point of view, the diphenic ligand is not good for magnetic exchange-coupling, as shown in compound **1**. However the occurrence of efficient Co−O−Co super-exchange pathways in compound **2** contributes to significant antiferromagnetic coupling between the cobalt(II) ions along the chains.

Experimental Section

General Remarks: The temperature variation of the magnetic moment between 2 K and 300 K was measured by using an MPMS*XL*-Quantum Design SQUID magnetometer at 200 Oe, in the field range corresponding to linear variation of magnetisation versus field. These data were corrected for sample diamagnetism by using Pascal's constants and for diamagnetism of the sample holder consisting of a gel cap. Magnetisation versus field data were recorded in the whole range between −5 and +5 T. UV/Vis-NIR studies were performed with a Perkin−Elmer Lambda 19 instrument (spectra recorded by reflection). FT-IR studies were performed with an ATI Mattson Genesis computer-driven instrument (0.1 mm thick powder samples in KBr). Thermogravimetric (TG) experiments were performed using a Setaram TG92 instrument (heating rate of 3 °C/min, air stream).

$Co_3(O_2CC_{12}H_8CO_2)_{2.5}(OH)(H_2O)_2$ (2): $C_3H_{255}Co_3O_{13}$ was synthesised by the hydrothermal method from $Co(NO_3)_2{\cdot}6H_2O$ (98% Aldrich), diphenic acid (1,1′-biphenyl-2,2′-dicarboxylic acid, 98% Across), and KOH (85%, SDS). The starting mixture corresponding to the molar composition 1:1.5:3.5:195 of $Co(NO_3)_2{\cdot}6H_2O$, $C_{14}H_{10}O_4$, KOH and H_2O was homogenized and transferred into a sealed 23 cm^3 hydrothermal bomb, walled with a Teflon liner, and heated at 170 °C for 74 h under autogenous pressure. The purple needle-shaped crystals obtained were washed with deionized water and rinsed with absolute ethanol [yield > 50% on the basis of $Co(NO_3)_2{\cdot}6H_2O$]. As mentioned above, some platelet-shaped crystals of the pink compound $C_{28}H_{32}Co_2O_{16}$ were also observed and pure compound **2** was isolated by manual separation of the largest crystals. The purity and the chemical formula were confirmed by elemental analysis and are consistent with the structural and magnetic findings: $C_{35}H_{25}Co_3O_{13}$ (830.4): calcd. C 50.63, H 3.03; found C 50.24, H 3.44. Oxidative pyrolysis (TG Analysis, heating in air from 20 to 700 °C at 3 °C/min, maintaining at 700 °C for 30 min to transform cobalt into Co_3O_4, and cooling to 20 °C at 10 °C/min: calcd. Co 21.3; found 21.6). IR (KBr pellet): $\tilde{\nu}$ = 3580 cm^{-1} (ν OH), 3429 (ν OH−O), 3056 (ν C−H), 1612 (δ H_2O), 1579 (ν C−C), 1540 (ν_{as} C=O), 1475 (ν C−C), 1442 (ν C−C), 1405 (ν_s C−O), 1267 (in plane δ_b C−H), 1151 (in plane δ_b C−H), 1108 (in plane δ_b C−H), 1049 (in plane δ_b C−H). UV/Vis (reflectance): see text.

X-ray Crystallographic Study: X-ray data collection was performed on a Nonius Kappa CCD at low temperature (T = 104 K) using a needle-shaped single crystal. 124314 Reflections were measured up to a resolution of 0.70 Å^{-1} and merged into 9210 unique reflections (R_{int} = 0.097). Crystal faces were indexed and a gaussian integration absorption correction[40] was applied (μ = 1.62mm^{-1}, T_{min} = 0.387, T_{max} = 0.798). The structure was solved by direct methods using SHELX,[41] the H atoms being localised in difference Fourier maps. The structure was refined by full-matrix least-squares on F^2 with anisotropic temperature factors for non H atoms and isotropic ones for H atoms and gave $R[F^2 > 2\sigma(F^2)]$ = 0.062, S = 0.85] final agreement factors. *Crystal data:* $C_{35}H_{25}Co_3O_{13}$, 830.32, monoclinic, *C2/c*, a = 19.370(1) Å, b = 14.5350(9) Å, c = 22.583(1) Å, β = 89.910(4)°, V = 6358.1(6) Å^3, Z = 8, D_x (g cm^{-3}) 1.727, Mo-K_α, 124314 reflections for cell parameters, μ (mm^{-1}) 1.618, temperature (K) 104(2), crystal form, needle, colour, purple, crystal size (mm) 0.14 × 0.14 × 0.52. *Data collection*: Diffractometer Nonius Kappa CCD; data collection method, ω scans; absorption correction, gaussian integration (DeTitta, 1985), T_{min} = 0.387, T_{max},= 0.798. No. of measured, independent and observed reflections, 124314, 9210, 4544; criterion for observed reflections, $I > 2\sigma(I)$; R_{int} = 0.097; θ_{max} (°) 30.03; range of h, k, l, $-27 \geq h \geq 27$, $0 \geq k \geq 20$, $0 \geq l \geq 31$; refinement on F^2, $R[F^2 > 2\sigma(F^2)]$ = 0.0623, $wR(F^2)$ = 0.1332, S = 0.852; no. of reflections and parameters used in refinement, 9210, 552; weighting scheme, $w = 1/[\sigma^2(F_o{}^2)]$, $(\Delta/\sigma)_{max}$ = 0.004, $\Delta\rho_{max}$ = 1.0984, $\Delta\rho_{min}$ = −1.074. CCDC-209800 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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