

Hydrothermal synthesis, structure and magnetism of square-grid cobalt(II)-carboxylate layered compounds with and without pillars

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The hydrothermal synthesis, single crystal X-ray structures and magnetic properties of two layered cobalt(II)-carboxylate complexes, ${}^2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(\text{O}_2\text{CCHCHC}_6\text{H}_5)_2]$ (**1**) and ${}^2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(\text{O}_2\text{CCHCHC}_6\text{H}_4\text{CO}_2)_{2/2}]$ (**2**), are described. Pale red crystals of $\text{Co}(\text{H}_2\text{O})_2\text{L}_2$, $\text{L} = \textit{trans}$ -cinnamate ($\text{C}_9\text{H}_7\text{O}_2^-$) (**1**) or $\text{L}_2 = 4$ -carboxycinnamate ($\text{C}_{10}\text{H}_6\text{O}_4^{2-}$) (**2**), were obtained at 120 °C. The structures consist of square-grid 2D-coordination polymeric sheets, $\cdots -\text{OCO}-\text{Co}(\text{H}_2\text{O})_2-\text{OCO}-\text{Co}(\text{H}_2\text{O})_2-\cdots$, separated by $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-$ for (**1**) or pillared by $-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-$ for (**2**). The magnetism was studied as a function of temperature and magnetic field. In both cases the magnetic moment decreases on lowering the temperature due to spin-orbit coupling and no interaction between cobalt ions. The data can alternatively be fitted to an unrealistic quadratic layer model for $S = 3/2$ without taking into account the effect of spin-orbit.

Introduction

Layered solids are an increasingly important class of materials of interest in the areas of sorption, separation and catalysis, as exemplified by layered double hydroxides, silicates and metal-dihalides, -dichalcogenides and -phosphates.¹ Transition metal coordination polymers are a newly added family to this list. Several families have been synthesised and characterised and their chemical and physical properties evaluated. The layers may comprise of a M–O network where the oxygen is part of a phosphate, oxalate, sulfate, silicate or hydroxide,² or a M–S network as in MPS_3 , or MS_2 ,³ or a M–X network as in MX_2 and A_2MX_4 .⁴ Only few of the layered M–O networks are known where the oxygen is from a carboxylate group.^{5–10} Here, we report two such examples, where the layer consists of a square-grid net of octahedral coordinated cobalt atoms connected by O–C–O bridges. In one case the layers are pillared by the organic backbone of the di-carboxylate and in the other they are separated by the mono-carboxylate. Similar nets have been observed for $\text{Co}(\text{H}_2\text{O})_2\text{terephthalate}$,⁶ $\text{Co}(\text{formamide})_2(\text{formate})_2$ ⁷ and $\text{Mn}(\text{H}_2\text{O})_2\text{acetylene-dicarboxylate}$,⁸ where the metal has octahedral coordination and for two compounds with the same layer topology but with tetrahedral coordinated cobalt and saturated alkyl di-carboxylate.^{9,10} Among these compounds, the Co-formate is the only one to exhibit long range magnetic ordering with a spontaneous magnetization due to non-collinearity of the sub-lattice magnetization. Other known ligands forming this kind of square-grid layers are thiocyanate and dicyanamide with manganese.^{11,12}

Metal carboxylate complexes have been the subjects of study for many years where the interest has focused on both structure and magnetism.¹³ The reactions of a carboxylic or di-carboxylic acid with a cobalt ion are known to result in several complexes depending on the concentration, the pH, the temperature and the synthetic method employed. The wide range of stable compounds is due to several parameters, *viz.* (a) the range of the coordination modes of the carboxylate ion (mono-dentate,

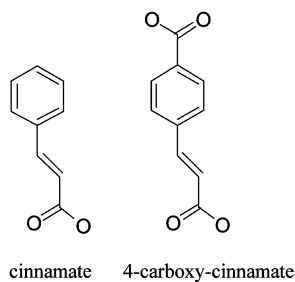
bi-dentate of *syn-syn*, *syn-anti*, and *anti-anti* types, and tri-dentate), (b) the stable coordination geometries (tetrahedral, pyramidal and octahedral) of Co(II) and (c) the presence of and the number of coordinated water or hydroxide.^{13,14} The isolation of single phases is a problem under certain conditions and polymorphism is an additional problem in some cases. Controlled hydrothermal synthesis is becoming one of the most reliable techniques for producing single phases of high crystallinity.¹⁵ For example, 1D, 2D and 3D compounds have been isolated and structurally characterised.^{16–18} Interestingly, some of the compounds are found to have cavities and channels with incorporated solvents, which may be removed without altering the framework.¹⁹

Among the layered phases, two families containing dicarboxylates have been isolated and fully characterised structurally, *viz.* (a) $\text{Co}_5(\text{OH})_8\text{L}_2 \cdot n\text{H}_2\text{O}$ which are ferrimagnets with Curie temperatures of 60 K²⁰ and (b) $\text{Co}_2(\text{OH})_2\text{L}_2$ which are metamagnets exhibiting large coercive fields at low temperatures.^{6,21} In both cases, the metals are arranged in a triangular lattice and the principal magnetic exchange is *via* the μ_3 -bridging hydroxide. The ferrimagnetic compounds were also obtained with several mono-carboxylates but they were poorly crystallised for crystal structure determination.²⁰ In contrast, no layered metamagnet has been isolated so far with a mono-carboxylate. A third family of layered compounds were also obtained with both mono- and di-carboxylates and coordinated water molecules instead of hydroxide.⁶ The resulting layers have different structural connectivity and magnetic topology which result in no long range magnetic ordering. The two examples presented here (see Scheme 1) belong to the latter family.

Experimental

Preparation of complexes

All chemicals (Tokyo Kasei Co. and Aldrich) were used as received without further purification.



Scheme 1 The molecular structures of *trans*-cinnamate and 4-carboxycinnamate.

Co(H₂O)₂(*trans*-cinnamate)₂ 1. Co(NO₃)₂·6H₂O (0.5 g, 0.0017 mol) was dissolved in distilled water (*ca.* 20 ml) and a solution of *trans*-cinnamic acid, C₆H₅CHCHCO₂H, (0.51 g, 0.0034 mol) and NaOH (0.13 g, 0.0033 mol) in distilled water (*ca.* 20 ml) was added. The mixture was placed in the Teflon liner of an autoclave, sealed and heated to 120 °C for 1 day. It was then allowed to cool to room temperature in a water bath. Pale red crystals were obtained which were washed with water and acetone and dried in air. Anal. calc. (%): CoC₁₈O₆H₁₈: C, 55.54; H, 4.66. Found: C, 54.67; H, 4.62. Infrared/cm⁻¹: 680m, 720 m, 780m, 880m, 980m, 1070w, 1250w, 1420s, 1450m, 1540s, 1580m, 1640s, 3020w, 3060w, 3080w, 3240mbr, 3340mbr, 3460mbr.

Co(H₂O)₂(4-carboxycinnamate) 2. Co(NO₃)₂·6H₂O (1.0 g, 0.0035 mol) was dissolved in distilled water (*ca.* 20 ml) and a solution of 4-carboxycinnamic acid, HO₂CC₆H₄CHCHCO₂H, (0.38 g, 0.002 mol) and NaOH (0.16 g, 0.004 mol) in distilled water (*ca.* 20 ml) was added. The mixture was placed in the Teflon liner of an autoclave that was then sealed and heated to 120 °C for 3 days. The bomb was placed in a water bath and allowed to cool to room temperature. Pink powder of Co₂(OH)₂carboxycinnamate and red crystals of Co(H₂O)₂carboxycinnamate were obtained. The crystals were first separated from the pink powder by decantation and then manually under a microscope. The crystals were finally washed with water and acetone and allowed to dry in air. Anal. calc. (%) for CoO₆C₁₀H₁₀: C, 42.13; H, 3.54. Found: C, 42.17; H, 3.50. Infrared/cm⁻¹: 485w, 492w, 560w, 704mbr, 800m, 862w, 890w, 986m, 1015w, 1112w, 1138w, 1182w, 1212w, 1255w, 1292w, 1368vs, 1410s, 1536vs, 1585vs, 1636s, 3316m, 3430msh.

Crystallography

For each compound, single crystals were glued onto the tip of a glass fibre. Intensity data were collected at room temperature on a Bruker SMART APEX CCD area detector (for **1**) and a Kappa-CCD Nonius diffractometer (for **2**) using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation (ω -scan mode). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The hydrogen atoms of the acid in **1** were located from difference Fourier maps and the hydrogen atoms of water were placed at ideal positions. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement for **1** was based on 1957 observed reflections [$I > 2.00\sigma(I)$] and 115 variable parameters; it converged to unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||\Sigma|F_o|$ of 0.043 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.127. The final cycle of full-matrix least-squares refinement for **2** was based on 1061 observed reflections [$I > 3.00\sigma(I)$] and 88 variable parameters; it converged to $R = 0.051$ and $R_w = 0.071$. No extinction corrections have been applied. Toward the end of the refinement of the structure of **2** the carbon atoms C(3) and C(4) appeared to be disordered and were finally refined as 50% occupancy at the two sites. A summary of the crystal data is collected in Table 1.

Table 1 Summary of crystal data

Compound	1	2
Formula	C ₁₈ H ₁₈ CoO ₆	C ₁₀ H ₁₀ CoO ₆
<i>M_w</i>	389.27	285.12
Crystal size/mm	0.1 × 0.1 × 0.05	0.15 × 0.1 × 0.1
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	36.564(5)	11.3236(4)
<i>b</i> /Å	6.4037(9)	6.6084(4)
<i>c</i> /Å	7.327(1)	7.2011(6)
β /°	92.101(4)	101.948(5)
<i>V</i> /Å ³	1714.5(4)	527.2(1)
<i>Z</i>	4	2
μ (Mo-Kα)/mm ⁻¹	1.032	1.642
No. reflections measured	1957	1317
No. observations	1394 [$I > 2.00\sigma(I)$]	1061 [$I > 3.00\sigma(I)$]
<i>R</i> (<i>R_w</i>)	0.043 (0.127)	0.051 (0.071)

CCDC reference numbers 182521 and 182522.

See <http://www.rsc.org/suppdata/dt/b2/b202995b/> for crystallographic data in CIF or other electronic format.

Physical measurements

Infrared spectra were recorded by transmission through KBr pressed pellets or thin films deposited on KBr plates by use of a MATTSON or a JASCO FTIR interferometer. The magnetic properties of the complexes were studied by Quantum Design MPMS-XL SQUID magnetometers in the temperature range 2–300 K and fields up to 5 Tesla. A Princeton Applied Research Vibrating Sample magnetometer was used to measure the isothermal magnetization in field up to 2 Tesla. X-Ray powder diffraction data were collected on a Siemens D-500 diffractometer equipped with Co-Kα ($\lambda = 1.789$ Å) radiation at room temperature.

Results and discussion

Preparation of the complexes

The choice of 4-carboxycinnamic acid (eight carbon atom bridge) was made so as to have a connector of length intermediate between terephthalic acid (six carbon atom bridge) and 4,4'-diphenyldicarboxylate (ten carbon atom bridge) for the study of the structural and magnetic properties of the metamagnets, Co₂(OH)₂L₂.^{6,21} *Trans*-cinnamic acid was chosen to remove the connection between the layers. We first observe that the blue–green ferrimagnets, Co₅(OH)₈L₂·*n*H₂O, are formed easily with the two acids. While we were able to synthesise the pink metamagnet Co₂(OH)₂(4-carboxycinnamate), we could not detect this phase with *trans*-cinnamic acid. In addition, good quality crystals of the di-aquo phase, Co(H₂O)₂L₂, have been obtained with both acids.

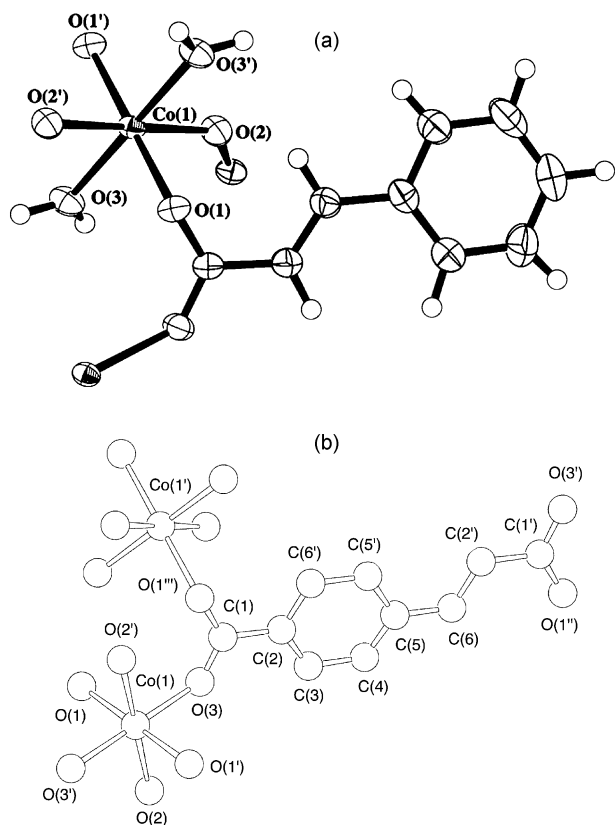
Crystal structures

The crystallographic data appear in Table 1 and a selection of the relevant bond lengths and angles are given in Table 2. The atom numbering schemes are shown in Fig. 1.

The structure of the two compounds consist of layers of a square-grid cobalt–oxygen net separated by the organic moieties. Each layer contains *trans*-Co(H₂O)₂ connected by four O–C–O bridges of the carboxylate groups (Fig. 2). The square arrangement is similar to that found in [Co(H₂O)₂BDC] (BDC = benzene 1,4-dicarboxylate or terephthalate). [Co(H₂O)₂BDC] crystallises in the monoclinic system *C2/c*, $a = 18.274(3)$, $b = 6.548(9)$, $c = 7.296(1)$ Å, $\beta = 98.6(3)^\circ$, $V = 862.5$ Å³ and $Z = 4$.⁶ Within the layer the shortest Co–Co distance in **1** is 4.9 Å and the second nearest is 6.4 Å. For **2** the shortest Co–Co distance is 4.9 Å and second nearest is 6.6 Å. These distances are comparable to those found in the terephthalate derivative that

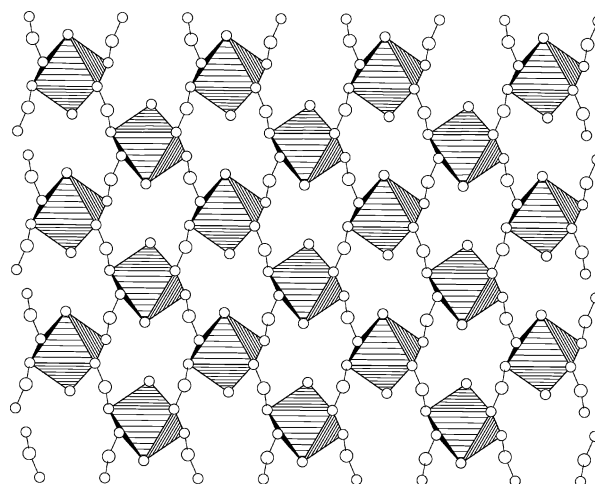
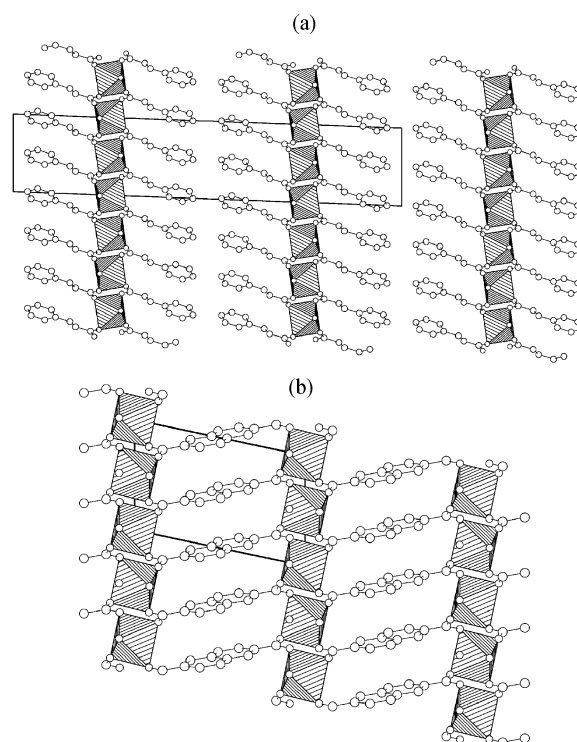
Table 2 Selected bond distances (Å) and angles (°) for **1** and **2**

1			
Co1–O1	2.096(2)	Co1–O3	2.091(2)
Co1–O2	2.066(2)		
O1–Co–O2	94.66(9)	O1–Co–O2'	85.34(9)
O1–Co–O3	92.28(9)	O1–Co–O3'	87.72(9)
O2–Co–O3	94.80(9)	O2–Co–O3'	85.20(9)
2			
Co–O1	2.107(3)	Co–O3	2.094(3)
Co–O2	2.083(3)		
O1–Co–O2	91.5(1)	O1–Co–O2'	88.5(1)
O1–Co–O3	87.3(1)	O1–Co–O3'	92.7(1)
O2–Co–O3	88.5(1)	O2–Co–O3'	91.5(1)

**Fig. 1** Coordination around the cobalt atoms and the adopted atom numbering for **1** (a), thermal ellipsoids at 50% probability, and **2** (b).

also contains Co in octahedral coordination; however, they are longer than those found in the anhydrous pimelate⁹ and glutarate¹⁰ derivatives that contain cobalt in tetrahedral coordination. This is consistent with the shortening of the Co–O bond lengths from octahedral (2.1 Å) to tetrahedral (1.9 Å) coordination.

The square-grid of cobalt is stabilised by covalent Co–O bonds and O–C–O bridging units. The Co–O bond lengths vary from 2.066 to 2.107 Å for the two compounds. These may be compared to the pimelate and glutarate derivatives that vary from 1.95 to 1.99 Å. It is to be noted that the structure is stable with or without the pillars. In the present compounds two bonded water molecules in the *trans*-positions complete the octahedron geometry. The Co–OH₂ bond lengths are 2.09 Å for **1** and 2.08 Å for **2**. The octahedra are considerably distorted with O–Co–O angles in the range 85.20(9)–94.80(9)°. To satisfy the constraint imposed by the rigid OCO bridges upon the layers, the octahedra are tilted from one another. The dihedral angles are 123.1° for **1**, 123.5° for **2**, and 125.1° for Co–(H₂O)₂BDC.⁶

**Fig. 2** View of a layer along the stacking axis (*a**-axis) showing the alternating orientation of the octahedra.**Fig. 3** View of the arrangement of the organic backbone in the galleries in **1** (a) and **2** (b). Due to the disorder of C(3) and C(4) the cinnamic backbone in **2** appears as naphthalene (see text).

One of the important structural differences between the two compounds is that the layers in **1** are separated by the cinnamate ion (Figs. 3a and 4a) and the layers in **2** are connected by the carboxycinnamate ion (Figs. 3b and 4b) in a similar fashion as that in the terephthalate derivative.⁶ To our knowledge the two examples are rare cases, which have been characterised structurally, where the same inorganic layer is separated by a carboxylate spacer in one case and connected in the other. The interlayer distance is 18.3 Å in **1**, 11.3 Å in **2**, and 9.1 Å in the terephthalate derivative. The increase from 9.1 Å for a bridging unit of six carbon atoms (terephthalate) to 11.3 Å for one with eight carbon atoms (carboxycinnamate) is as expected. This is comparable to those observed for the Co₂(OH)₂L₂ series, 9.9 Å for L₂ = terephthalate and 12.1 Å for L₂ = carboxycinnamate.²¹ However, the large difference in interlayer distance between **1** and **2** is due to (a) the presence of twice the number of acid

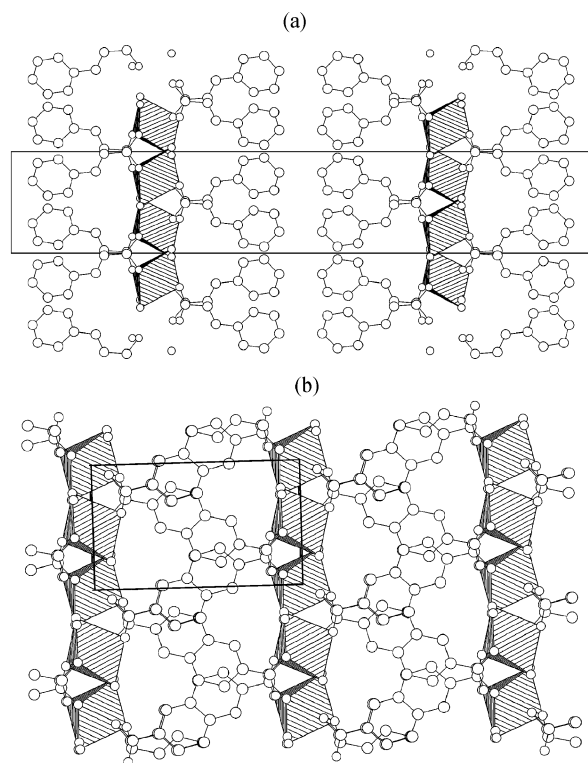


Fig. 4 View of the zig-zag arrangement of the aromatic rings within the galleries for **1** (a) and **2** (b).

units in **1** and (b) the non-interdigitation of the cinnamate ion in **1** due to crowding and consequently to the repulsion of the benzene rings. It is interesting to note that in neither of them is solvent water molecule included in the lattice, although the synthesis is performed in water. This may be due to the lack of available polar groups for hydrogen bond formation. The extent of void space in **1**, as suggested by the lack of residual electron density in the difference Fourier maps, compared to **2** can be seen in the calculated densities, 1.51 g cm^{-3} for **1** and 1.81 g cm^{-3} for **2**. It is also to be noted that these densities are still lower than that of the terephthalate derivative (2.00 g cm^{-3}). It would be interesting to check if the layers in **1** can be further separated by intercalation of neutral compounds.

Magnetic properties

The magnetic properties of compounds **1** and **2** were studied as a function of temperature (2–300 K) in a fixed magnetic field and as a function of field up to 5 Tesla at different fixed temperatures; the data for **2** are shown in Figs. 5 and 6. The moment decreases in both cases as the temperature of the sample is lowered. The data above 150 K can be fitted to a Curie–Weiss function with Curie constants, $2.78 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** and $2.95 \text{ cm}^3 \text{ K mol}^{-1}$ for **2** and Weiss constants -24.05 K for **1** and -18.6 K for **2**. The effective magnetic moment (μ_{eff}) per cobalt ion [$4.54 \mu_{\text{B}}$ (**1**) and $4.7 \mu_{\text{B}}$ (**2**)] is consistent with those expected for octahedral cobalt(II). The values are typical for cobalt(II) ion in an octahedral environment with an enhanced moment due to orbital contribution and a lowering of the moment at low temperatures due to the effect of spin–orbit coupling.^{22,23} A slight discontinuity is observed in **1** around 50 K due to unavoidable contamination from small particles of the ferrimagnetic compound, $\text{Co}_5(\text{OH})_8(\text{cinnamate})_2 \cdot n\text{H}_2\text{O}$ which is not even seen under a microscope!

The magnetic properties of the square-grid layered compounds of cobalt referred to above have all been studied as a function of temperature and magnetic field.^{7,9,10} They were found to be quite different. For example, the two compounds with tetrahedral coordinated cobalt centres exhibit maxima

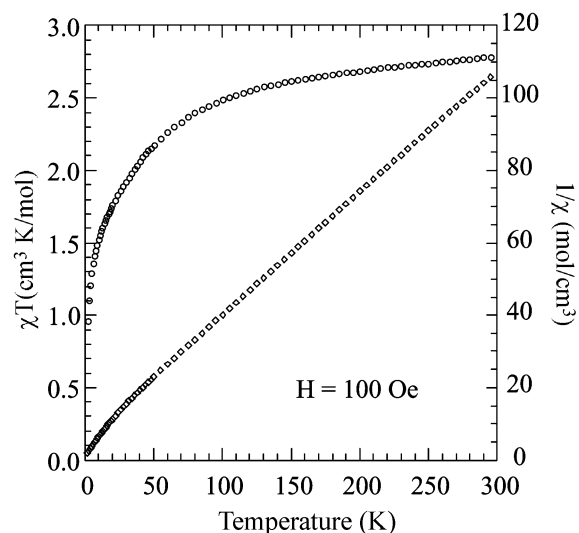


Fig. 5 Temperature dependence of the product of susceptibility and temperature (circles) and the inverse susceptibility for **2** (diamonds).

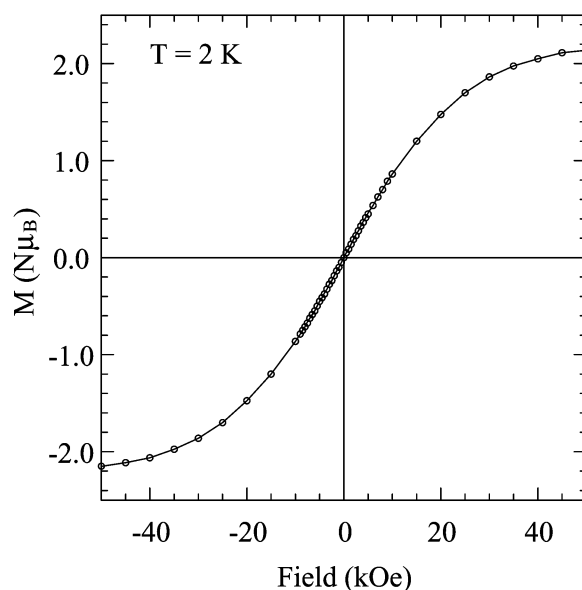


Fig. 6 Isothermal magnetization of **2** at 2 K; line is a guide to the eye.

around 15 K.^{9,10} In both cases, the high temperature behaviour is described as paramagnetic with Weiss constants of $-23 \pm 2 \text{ K}$. On the one hand, a small rise in the susceptibility below 10 K for the pimelate compound and the appearance of a weak hysteresis at 4.2 K were interpreted as being due to a small canting.⁹ On the other hand, the rise at low temperatures in Co-glutarate was associated with the presence of a paramagnetic impurity.¹⁰ In contrast, the cobalt-formate compound exhibits a field dependent magnetization below 9 K and a clear hysteresis loop that were associated with canting.⁷

The temperature dependence of the magnetic susceptibility of Co-glutarate in the range 15–300 K has been modelled by use of Lines' model for a quadratic layer antiferromagnet of $S = 3/2$.^{10,24} This model was also used by Rettig *et al.* for Co-formate. Although reasonable agreement was obtained, the latter authors argued against such a model on the grounds that it ignores the effect of spin–orbit coupling. Having clean sets of data for **2** and $\text{Co}(\text{H}_2\text{O})_2\text{BDC}$ we attempted to fit the data with the Lines' model.⁷ It gives visually good fits but the values of J and g vary enormously depending on the range of temperature over which the fit was performed. For example the g -value varies from a modestly acceptable 1.9 to an unrealistic 12. The instability of the fits is due to the lack of any maximum in the

temperature dependence of the susceptibility results in several possible solutions.²⁵ The use of the function given by Mabbs and Machin²² that take into account the effect of spin-orbit coupling does not quite represent the observed data. Whether this is due to severe distortion of the cobalt coordination from exact octahedral for which the function was worked out is not clear.

The isothermal magnetization at 2 K (Fig. 6) exhibits a continuous increase to a saturation value of $2.2 \pm 0.2 \mu_B$ per cobalt ion. No hysteresis was observed. The curve is consistent with that expected for a Brillouin function. Its saturation value is within the range expected for free cobalt ion with an effective $S = 1/2$ and anisotropic g -values. It further confirms that the cobalt ions do not interact.

Conclusion

Three distinct layered phases have been identified in the hydrothermal reaction of Co(II) and terephthalate or carboxycinnamate in alkaline media; a blue-green ferrimagnet $[\text{Co}_5(\text{OH})_8\text{L}_2 \cdot n\text{H}_2\text{O}]$, a light pink metamagnet $[\text{Co}_2(\text{OH})_2\text{L}_2]$, and a pale red paramagnet $[\text{Co}(\text{H}_2\text{O})_2\text{L}_2]$. Interestingly, the metamagnetic phase is not stabilised by mono-carboxylate. The two examples presented here are rare cases for which we have demonstrated structurally that the inorganic layers can be either separated by spacers or pillared by connectors. The bent O–C–O bridges are found to be poor exchange pathways for long range magnetic ordering to occur compared to the linear N–C–N bridges found in dicyanamide complexes.^{26–29}

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