Ferromagnetism in Triangular Cobalt(II) Layers: Comparison of Co(OH)₂ and Co₂(NO₃)(OH)₃

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This paper deals with correlations between structural and magnetic properties of two layered parent compounds, $Co(OH)_2$ and $Co_2(NO_3)(OH)_3$, which mainly differ by their interlayer distances. Measurements of magnetization, magnetic susceptibility, and specific heat show the occurrence of phase transitions at nearly the same temperatures, and this is explained by strong anisotropic in-plane interactions between cobalt(II) ions. Using HTS expansion for a triangular 2D lattice and numerical computations, the in-plane ferromagnetic interactions are shown to be $J = 9.2$ K for $Co(OH)_2$ and 7.4 K for $Co_2(NO_3)(OH)_3$. In the ordered state, both compounds exhibit metamagnetic behavior with critical fields mainly related to interplane interactions. A spin anisotropy crossover (from XY to Ising) is suggested to explain the magnetic findings above and below T_c.

I. Introduction

Two-dimensional triangular arrays of transition metal ions exhibit a large variety of magnetic properties which depend on the spin value, the nature of the exchange coupling (Ising, Heisenberg, XY, or a mixture of them), the sign of the exchange integral(s), and other factors. An authoritative survey of the thermodynamics and experimental behavior of two-dimensional magnets has recently been reported by De Jongh.[1] As emphasized in this book, very few compounds exhibit triangular planar networks which would allow experimental investigations of the proposed models. For this purpose, we have investigated the family of transition metal hydroxonitrates $M(OH)_{2-x}(NO_3)_x \cdot mH_2O$ (M = Co, Ni, Cu, ...) compounds which are characterized by a cation ordering in two-dimensional triangular structures. These compounds have been thoroughly studied from a structural point of view, in particular by Louër et al.,[2] who proposed a classification of the different structural types on the basis of the hydroxides $M(OH)_2$. The compounds crystallize in stacks which are built up from $[M(OH)_2]$ sandwich layers made of one metal plane located between two hydroxide sheets. In $M(OH)_2$ hydroxides, the metal ions (in O_h symmetry) form regular triangular arrays (Figure 1a). In turn, the structure of the hydroxonitrates $M(OH)_{2-x}(NO_3)_x \cdot mH_2O$ is derived from the parent compound by replacing some $(OH)^-$ ions by oxygen atoms belonging to nitrate groups (Figure 1b). The dimension of the latter implies a large increase of the interplanar distance along the c axis.

In this work, we compare the properties of the two-dimensional parent compounds β-Co(OH)₂ and Co₂(NO₃)(OH)₃. Only few results have been reported on the magnetic properties of β-Co-(OH)₂.[3] From magnetic susceptibility and magnetization measurements, it has been shown that this compound exhibits an antiferromagnetic transition at $T_c = 12.3$ K, with metamagnetic behavior in the ordered state in relatively low fields. To explain this behavior, it was assumed that cobalt(II) ions are coupled ferromagnetically within triangular planes and antiferromagnetically between adjacent ones. Further, it was predicted that,
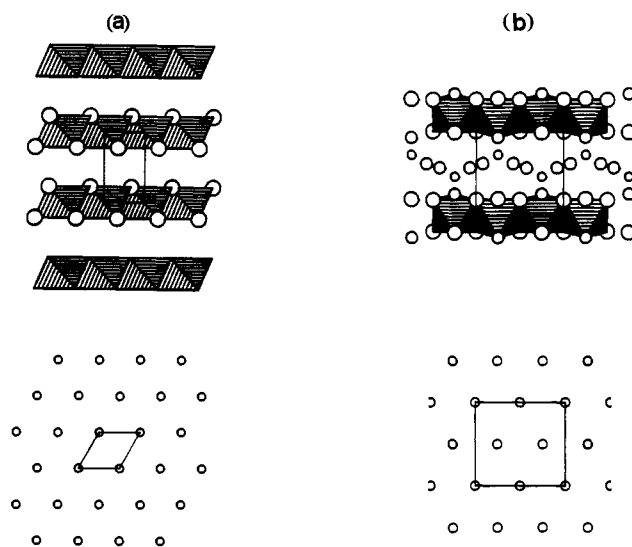

Figure 1. Structures of Co(OH)₂ (a) and Co₂(NO₃)(OH)₃ (b) showing the stacking of cobalt(II) layers along c axis and the unit cell in (a,b) plane.

in the ground-state, the spin axis is parallel to the metal layer. On the other hand, a heat capacity anomaly has been observed at the transition temperature by Sorai et al.[4] Using the triangular 2d Ising model for $S = 1/2$, the in-plane exchange interaction $(J/k = 3.19$ K) was deduced from the critical temperature, $T_c = 11.6$ K, by applying the results of the treatment developed by Houtappel.[5]

Cobalt(II) hydroxonitrates have been extensively investigated from crystallographic viewpoint by Feitknecht et al.[6] The authors report the existence of a double-layer compound, namely type III Co₇(NO₃)₂(OH)₁₂, and a single-layer compound, namely type II Co₂(NO₃)(OH)₃, depending on the conditions of synthesis. Both compounds exhibit an ordered (α) and a disordered (β) form. From X-ray diffraction patterns, it appears that β-Co₂(NO₃)-(OH)₃ exhibits an hexagonal structure with an enhancement of the interlayer distance with respect to β-Co(OH)₂ (c = 6.95 Å for the former and 4.65 Å for the latter[7]). The ordered phase,

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α, exhibits the same XRD pattern as β, as well as additional weak lines which denote a higher order degree. Feitknecht[8] described the structure by assuming a monoclinic unit cell, with $a = 5.50$ Å, $b = 6.25$ Å, $c = 6.93$ Å, $\beta = 93.33°$, and space group $P2_1/m$. It could be assumed that β-$Co_2(NO_3)(OH)_3$ is isostructural with the copper(II) hydroxonitrate ($a = 5.61$ Å, $b = 6.09$ Å, $c = 6.93$ Å, $\beta = 94.48°$, $P2_1/m^9$), as suggested by the existence of a solid solution. In fact Glibert et al.[10] and Markov et al.[11] reported substitution of Co(II) ions into $Cu_2(NO_3)(OH)_3$ up to a ratio Co/Cu ≈ 1, only. Indeed, $Co_2(NO_3)(OH)_3$ was described by Markov et al.[11,12] in terms of a hexagonal cell, $a = 3.17$ Å and $c = 6.95$ Å, with a turbostratic disorder along the c axis.

Since, to our knowledge, no magnetic study of $Co_2(NO_3)$-$(OH)_3$ has been reported, we discuss in this paper the magnetic properties of this cobalt(II) compound and compare these properties to those of the parent compound β-$Co(OH)_2$. The aim is to determine to what extent these materials are good candidates for testing 2D triangular lattice models. First, we show the structural similarity of both compounds from XRD, transmission electron microscopy, thermal, and IR analyses. Then, the magnetic properties are investigated through magnetic and specific heat measurements. Finally, the values of the exchange constants and critical exponents are discussed.

II. Experimental Section

The title compounds were synthesized from $Co(NO_3)_2$·$6H_2O$. Aqueous solutions were carefully deoxygenized with a nitrogen gas flow. Co-$(OH)_2$ was precipitated by adding a 1 M aqueous solution of Co-$(NO_3)_2$·$6H_2O$ into 1 M KOH. The precipitated hydroxide was kept in the solution under nitrogen for 2 h and then washed with ice water and absolute ethyl alcohol. After alcohol evaporation, the final product was dried in a desiccator under primary vacuum. The cobalt(II) hydroxonitrate was obtained by following the method reported by Glibert[10] and Markov.[11,12] Then 1 M LiOH was added slowly into a 3.5 M $Co(NO_3)_2$·$6H_2O$ boiling solution to yield a Li/Co = 1.5 molar ratio. The pH, at a constant value of 4.5, was followed using a digital pH-meter (Metrohm-Herisau E532) and a high-temperature electrode (Ingold 405-60-57). The precipitated cobalt(II) hydroxonitrate was washed with ice water and absolute ethyl alcohol and then dried at 40 °C for 12 h under air. Complexometric analysis of the metal element and thermogravimetric measurements confirmed the chemical formula $Co_2(NO_3)(OH)_3$·$0.03H_2O$.

Differential thermal (DTA) and thermogravimetric (TGA, DTG) analyses were performed using a Setaram TGDTA-92 thermo-balance. The XRD characterizations were carried out using a Siemens D500 diffractometer (Co Kα_1 = 1.788 97 Å) with NaCl being used as an internal standard. The programs TREOR,[13] DICVOL91,[14] and NBSAIDS83[15] were used for automatic indexing of the patterns and for refining of the cell parameters. A Philips EM 300 (100 kV) transmission electron microscope was used for some selected area electron diffraction (SAED) studies. Magnetic susceptibility and magnetization data were recorded from powder samples by using a Faraday-type fully automated magnetic equipment (Manics) in the range 4–300 K, and a SQUID magnetometer (Métronique) in the range 1.2–200 K. Specific heat measurements were done using a quasi-adiabatic method.[16] The IR spectra of both compounds

were obtained with Bruker Fourier interferometers, Models IFS 66 and FIR 2, in the ranges 400–4000 cm^{-1} (pelleting with KBr) and 90–500 cm^{-1} (with polypropylene), respectively.

III. Results

Structural Characterization. The XRD pattern of $Co(OH)_2$ agrees well with the structural features of the β-type reported in the literature.[7] In turn, the cobalt hydroxonitrate corresponds to the α form of $Co_2(NO_3)(OH)_3$ proposed by Feitknecht[6] (supplementary material). It may be indexed with a monoclinic cell, $a = 5.531(2)$ Å, $b = 6.2999(8)$ Å, $c = 6.964(1)$ Å, $\beta = 93.18(3)°$, and $V = 242.32(7)$ Å^3 ($P2_1/m$, $M(20) = 26.4$). From TEM observations, it appears that the hydroxonitrate crystallizes in a platelet-like shape which corresponds to the (a,b) plane, while SEAD patterns exhibit the (pseudo)hexagonal symmetry of the basal (cationic) plane. No turbostratic disorder characteristics were observed.

IR spectra of $Co(OH)_2$ (supplementary material) display a metal–oxygen peak at ca 300 cm^{-1}, which is characteristic of β-$Co(OH)_2$ when compared with $CoO(OH)$.[17] As reported earlier,[17] $Co(OH)_2$ exhibits a sharp absorption peak at 3630 cm^{-1}, followed by a broad band from 3550 to 3100 cm^{-1}. These bands indicate the presence of free and hydrogen-bonded hydroxyl groups. $Co_2(NO_3)(OH)_3$ exhibits a more complex IR spectra. However it is obvious that the main characteristics of $Co(OH)_2$ are still present. The assignment of the observed absorption bands were made according to previous results.[18-21] Compared with $Co(OH)_2$, a more intense absorption peak is found at 3520 cm^{-1} ($\nu(OH)$–OH). Nitrate absorption bands arise at 1490 cm^{-1} (ν_4), 1385 and 1320 cm^{-1} (ν_1), 1000 cm^{-1} (ν_2), 700 and 730 cm^{-1} (ν_5), and 805 cm^{-1} (ν_6). There is no band at 495 cm^{-1}, but a new band arises at 630 cm^{-1} ($\nu(Co$–$OH)$). The very complex far-infrared spectrum in the 400–300 and 170–270 cm^{-1} ranges may be associated with metal–oxygen bonds, involving oxygen atoms of $(NO_3)^-$. These infrared results are consistent with bridging bidentate coordination of the nitrate groups.

Thermal Analysis. From DTA–TGA data, it appears that Co-$(OH)_2$ decomposes in two steps under air (supplementary material) after elimination of some adsorbed water between 50 and 100 °C (0.6% in mass). The first weight loss (150 °C) corresponds to dehydration of the compound accompanied by an (exothermic) oxidation of divalent cobalt. The decomposition process proceeds with a further weight loss step at 250 °C. Stoichiometric Co_3O_4 is obtained at 700 °C. Under an inert gas, there is no exothermic peak (DTA) and a one step dehydration is obtained at ca. 200 °C.

In the case of the cobalt(II) hydroxonitrate, our results are consistent with those reported in refs 11 and 12. Elimination of some water (0.3% in mass) is observed in the range 50–100 °C. Then, $Co_2(NO_3)(OH)_3$ decomposes endothermally in one step at 195 °C. The DTG and DTA peaks are very sharp, which points to a very fast decomposition. Stoichiometric Co_3O_4 is obtained at 700 °C. No exothermic DTA peak is observed, indicating that the oxidation process is different from that of β-$Co(OH)_2$. This is due to the presence of nitrate groups which constitute an intrinsic oxidative agent for the Co(II) ions.

Magnetic Measurements. The temperature dependence of the magnetic susceptibility (recorded at 500 Oe) and high field magnetization of $Co(OH)_2$ are plotted in Figures 2 and 3. These data well agree with previously reported results.[3] As shown in Figure 2, χT exhibits upon cooling a quasi-constant value between 300 and 100 K ($\chi T = 3.5$ emu·K/mol) and then a slight decrease

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(16) The calorimeter was designed by R. Kuentzler and Y. Dossmann (Strasbourg) for measurements in the temperature range 0.9–40 K. It is made of an adiabatic chamber with a saphir sample holder, equipped with a Ge resistance thermometer and an evaporation deposit Cr/Ti heater. The sample holder is suspended with nylon threads. The accuracy of the measurements is better than 1%.

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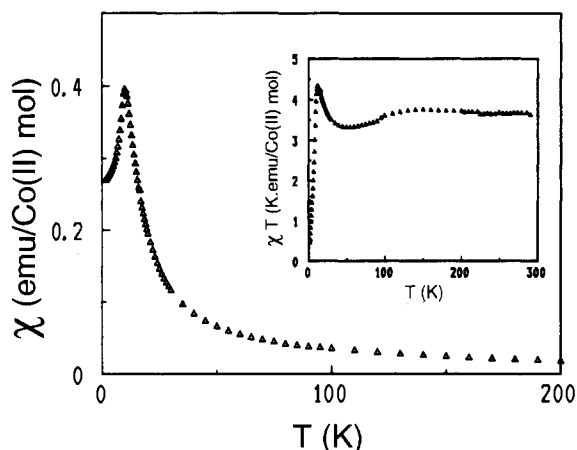
Figure 2. Temperature dependence of the magnetic susceptibility and the χT product for Co(OH)$_2$, in an applied field of $H = 5 \times 10^{-2}$ T.
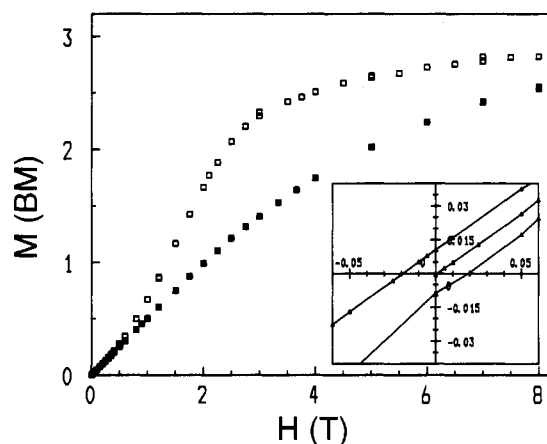

Figure 3. Field-dependent magnetization of Co(OH)$_2$ at 4.5 K (open squares) and 15 K (full squares). The inset focuses on the low-field measurements.

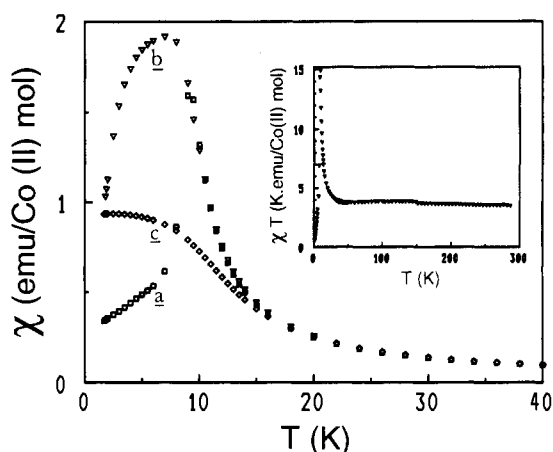**Figure 4.** Temperature dependence of the magnetic susceptibility and χT product of Co$_2$(NO$_3$)(OH)$_3$ for various applied fields: (a) 33×10^{-4}, (b) 0.2, and (c) 1 T.
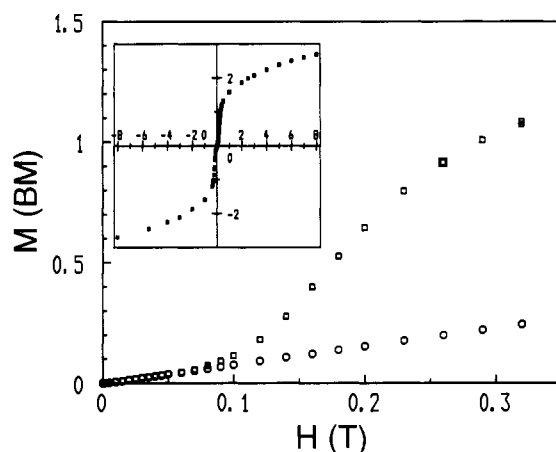

Figure 5. Field-dependent magnetization of Co$_2$(NO$_3$)(OH)$_3$ at 4.5 K (squares) and 15 K (circles). The high-field magnetization measurements at 4.5 K are displayed in the inset.

down to 40 K due to the spin–orbit coupling effect for Co(II) ion, stabilizing a Kramers doublet ground-state. At lower temperatures, a significant increase of χT is observed up to a sharp maximum ($T_{\chi T max} = 10.0$ K (± 0.1 K)), and then a drop to zero is seen on further cooling. Such behavior is characteristic of ferromagnetic in-plane interactions between cobalt(II) ions, as emphasized by Takada et al.[3] High-field magnetization measurements were performed at 4.5 and 15 K (Figure 3). M(H) shows a gradual increase with a typical metamagnetic transition in the ordered state for $H_c = 1.5$ T and a saturation at ca. 2.9 μ_B which agrees with the expected value for cobalt(II) ion.

A similar behavior is observed for Co$_2$(NO$_3$)(OH)$_3$. The magnetic susceptibility plotted vs temperature in Figure 4 shows a clear dependence on applied field. At low field ($H = 33$ Oe), χ exhibits a sharp maximum at $T_c = 9.8$ K (± 0.1 K) close to the value obtained for Co(OH)$_2$. $\chi T = f(T)$, displayed in the inset, shows a constant value at high temperature (namely 3.6 emu·K/Co^{II}), a strong increase for $T < 30$ K, and a drop to zero below T_c. Note that such a behavior is very similar to that of the cobalt hydroxide. Further, magnetization measurements (Figure 5) indicate a metamagnetic behavior at 4.5 K with a critical field $H_c = 0.17$ Tesla. Measurements in a very high field (up to 8 T) do not allow one to achieve complete saturation of magnetization, but an asymptotic value of 2.87 μ_B/Co^{II} mol is deduced, in agreement with data for Co(OH)$_2$.

The results of specific heat measurements on Co(OH)$_2$ and Co$_2$(OH)$_3$(NO$_3$) are plotted in the range 1.5–40 K in Figures 6 and 7. Both compounds exhibit an anomalous peak with the maximum located at 11.6 K (± 0.2 K) for the hydroxide and 8.7 K (± 0.1 K) for the hydroxonitrate. It can be noted that the peak

is broader for Co(OH)$_2$. By comparison with the magnetic susceptibility maxima (10.0 and 9.8 K, respectively), these peaks may be related to the stabilization of a long-range magnetic ordering. The results for Co(OH)$_2$ agree well with those of Sorai et al.,[4] who reported a λ-type anomaly at 11.6 K. At higher temperatures, the increase of C_p is mainly due to the lattice contribution; however, we cannot neglect the contribution of short-range 2D magnetic interactions which are expected to give rise to a Schottky-type anomaly above T_c. Accordingly, the high-temperature data ($T > 15$ K) have been fitted to the relationship $C_p = AT^{-2} + BT^3$, where the first term is ascribed to the 2D magnetic correlations (Schottky tail) while the second term deals with the lattice contribution. After subtracting the latter (full line in Figures 6 and 7), we get the specific heat of magnetic origin (dotted line). The maximum observed around 25–30 K, in particular with the hydroxonitrate, suggests that a large amount of short-range order is present, as might be expected from the structural features. However, due to the large uncertainties on lattice contributions in this temperature region, such an analysis must be considered with much caution.

IV. Discussion

First, it may be pointed out that the IR spectra agree well with the general description of the layered cobalt(II) hydroxide and hydroxonitrate.[2] The refined cell parameters of the hydroxonitrate are very close to those of Cu$_2$(NO$_3$)(OH)$_3$. However, the refinement figure of merit is not very good because of the different number of observed diffraction lines as compared to the calculated ones. This may not be explained here by a turbostratic disorder
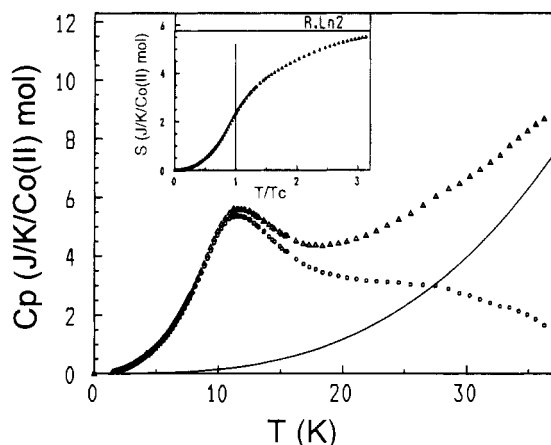
Figure 6. Temperature dependence of the specific heat of $Co(OH)_2$. The full line and dotted line represent the lattice and magnetic contributions, respectively. The magnetic entropy is plotted in the inset.
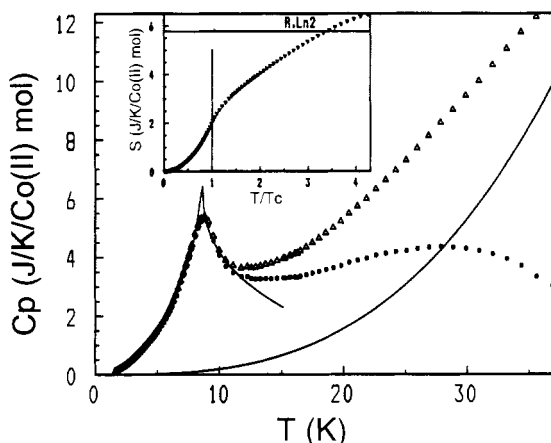

Figure 7. Temperature dependence of the specific heat of $Co_2(NO_3)$-$(OH)_3$. The full line and dotted line represent the lattice and magnetic contributions, respectively. The best fit of the λ-type anomaly (see text) is also drawn. The magnetic entropy is plotted in the inset.

but could be related to the degree of order of the nitrate groups. We may assume that $Co_2(NO_3)(OH)_3$ corresponds to an intermediate case between $Ni_2(NO_3)(OH)_3$,[22] characterized by statistically distributed $(NO_3)^-$ ions, and $Cu_2(NO_3)(OH)_3$ which shows a complete ordering of the nitrate ions. To compare the two title compounds, note that the cell parameters of cobalt hydroxonitrate derive easily from those of β-$Co(OH)_2$ ($a_0 = 3.17$ Å, $c_0 = 4.65$ Å, space group $R\bar{3}m$) by considering the ortho-hexagonal unit cell $a = 3^{1/2}a_0 = 5.49$ Å and $b = 2a_0 = 6.34$ Å. Also the SAED patterns confirm the hexagonal symmetry of the cationic planes in $Co_2(NO_3)(OH)_3$ as in $Co(OH)_2$. The in-plane $Co(II)$–$Co(II)$ distances, related to a (or b) parameters, are very close in both structures, while the periodicities c of the stacking differ very much ($c = 1.5c_0$). So, the essential difference between these two compounds is a larger distance between successive Co-(II) layers in $Co_2(NO_3)(OH)_3$ with respect to $Co(OH)_2$.

Clearly, the susceptibility and magnetization results indicate for both compounds two regimes, corresponding to short-range ($T > T_c$) and long-range ($T < T_c$) magnetic correlations between cobalt(II) ions. At high temperature, ferromagnetic in-plane interactions dominate the magnetic properties, as evidenced by the sharp increase of χT when approaching the ordering temperature. Thus, the title compounds may be viewed as good prototypes of 2D triangular ferromagnets, the properties of which closely depend on the spin dimensionality. At low temperature, an important problem concerns the lattice dimensionality, in other words, to what extent the thermodynamic properties of the cobalt-

(II) layers are affected by the weak interlayer interactions which are always present. Some insight will be given in the following discussion.

Cobalt(II) salts provide the most thoroughly studied examples of layered Ising (uniaxial anisotropy) or XY-type (planar anisotropy) systems. However, it should be noted that most of them show antiferromagnetic in-plane interactions.[23,24] Referring to the magnetic structure of $CoBr_2$ and $CoCl_2$, Takada et al.[3] inferred that in $Co(OH)_2$ the single-ion anisotropy induces the spins to lie in the c-plane rather than along the trigonal axis. In fact, this was not clearly shown by neutron diffraction or single-crystal magnetization measurements. Further, it can be noted that the trigonal field splitting is small, and may even change in sign from compound to compound, as observed for $FeCl_2$ and $Fe(OH)_2$.[25] For the former, the spins are aligned parallel to the trigonal axis, while they are in the c-plane in the latter.

In the case of the cobalt(II) hydroxonitrate, it can be assumed that the presence of $(NO_3)^-$ groups breaks the trigonal symmetry, thus promoting a preferential axis within the easy XY plane. Accordingly, such a system may constitute a good example of pseudo-Ising type anisotropy in a predominantly XY-type system.

As a result of the combined action of crystal-field and spin-orbit coupling, the lowest multiplet of $Co(II)$ is well approximated by an effective spin $S = \frac{1}{2}$, with highly anisotropic properties.[26] The spin Hamiltonian describing the in-plane exchange interactions may be written as

$$H = -J_{\parallel}\sum S_{iz}S_{jz} - 2J_{\perp}\sum(S_{ix}S_{jx} + S_{iy}S_{jy}) \quad (1)$$

where $J_{\parallel}$ and $J_{\perp}$ are the exchange constants for the Ising and XY limits. Camp and Van Dyke[27] have derived, for the Ising model, the magnetic susceptibility of the $S = \frac{1}{2}$ triangular 2D-lattice, by using a high-temperature series (HTS) expansion. They obtained the expression

$$\chi = Ng^2\mu_B^2/4kT\sum a_n(J/kT)^n \quad (2)$$

where the coefficients a_n are listed in Appendix 1. Using the Padé approximant technique, it was shown that the susceptibility obeys a power law variation $\chi = (1 - T/T_c)^{-7/4}$ in the vicinity of the critical (Curie) temperature given by $J/kT_c = 1.0986$.[28]

A classical spin model has been developed for the triangular lattice with XY anisotropy, but such a treatment is questionable in the present case. Indeed, if a diverging susceptibility is predicted at the Kosterlitz–Thouless transition (T_{KT}), no singularity of the specific heat is expected for the classical 2D XY model. Further, no rigourous expression of the susceptibility is available for the XY triangular lattice with interacting quantum spins $S = \frac{1}{2}$.

An analysis of the magnetic data of both $Co(II)$ compounds (for $T_c < T < 30$ K) has been performed on the basis of the $S = \frac{1}{2}$ 2D Ising model.

Two procedures were followed in the fitting process. In the first analysis, interplane exchange interactions were neglected, and the data were fitted with expression 2, by using g and J as adjustable parameters. The results giving the best agreement between theory and experiment are listed in Table I. In the second analysis, we introduced the influence of inter-planar interactions within the molecular field approximation. Due to the increase in the value of the χT product of the $Co(II)$ layers upon cooling, an interlayer cooperative effect is expected at very low temperature, so that the two-dimensional approximation may be questionable. Clearly, the interaction between adjacent layers will depend on the interlayer distance, namely the c parameter,

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Table I. Values of the Parameters g, J, and j Obtained from the Best Fits of the Experimental Magnetic Susceptibility Data Using HTS Expansion or Numerical Analysis

compound	dimen-sionality	HTS expansion analysis			numerical analysis		
		g	J (K)	j (K)	g	J (K)	$\lvert j\rvert$ (K)
Co(OH)$_2$	2D	5.79	2.1				
	2D/3D	5.09	9.2	−2.57			
Co$_2$(OH)$_3$(NO$_3$)	2D	5.15	6.7				
	2D/3D	5.11	7.4	−0.23	5.36	9.9	<10^{-2}
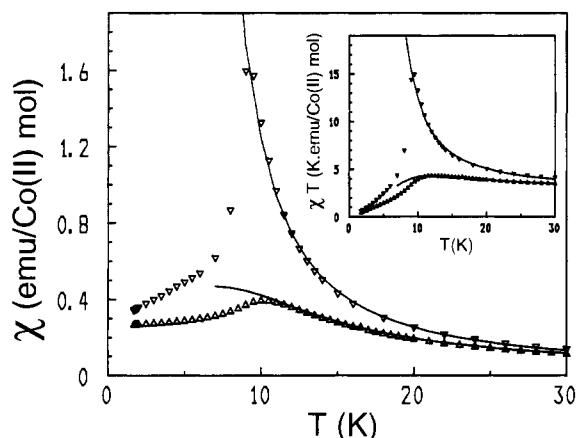
Figure 8. Best fits of the magnetic susceptibility and χT product of Co(OH)$_2$ (△) and Co$_2$(NO$_3$)(OH)$_3$ (▽) using the HTS expansion derived for the $S = {}^1/_2$ Ising triangular layer.[27]

so that it must be more significant for Co(OH)$_2$ than for Co$_2$-(NO$_3$)(OH)$_3$. Using the modified expression of the susceptibility[29]

$$\chi' = \chi/(1 - zj\chi/Ng^2\mu_B{}^2) \qquad (3)$$

where j represents the interlayer exchange coupling, a very good description of the magnetic susceptibility was obtained from the parameters listed in Table I (see Figure 8). From the above results, the following conclusions may be reached. (i) The in-plane ferromagnetic coupling (J) cannot be determined unambiguously with a simple two-dimensional model. When isolated Co(II) layers are considered, the obtained J value is significantly smaller for Co(OH)$_2$ than for Co$_2$(NO$_3$)(OH)$_3$, while the in-plane metal distances are very close. By the introduction of interplane interactions, it appears that J values become very similar to each other in both systems. (ii) The two-dimensional character is much less pronounced for Co(OH)$_2$ than for Co$_2$(NO$_3$)(OH)$_3$, as deduced from the j values. This result is confirmed by the critical fields (H_c) at which both systems undergo a metamagnetic transition. Assuming that the inter-planar interaction is related to H_c through the relation $j = g\mu_B H_c/2S$, we obtain $j = -2.0$ K for Co(OH)$_2$, and $j = -0.2$ K for Co$_2$(NO$_3$)(OH)$_3$, in good agreement with the above results, which are summarized in Table I.

The difference in H_c values measured at 4.5 K for the two compounds is thus well understood from the difference between the interlayer interactions. More surprising is the similarity of transition temperatures, which may be due to the pronounced anisotropic character of Co(II) compounds. Indeed, for Ising-like layered systems, it is well established that a long-range magnetic ordering takes place at a finite temperature.[28]

An alternative way to describe the magnetic properties consists of performing exact calculations for finite equilateral triangular units. The number of spins involved in a triangular unit increases rapidly with the number of rows (L), according to $N_s = {}^1/_2(L +$

(29) *Magneto-Chemistry*; Carlin, R. L., Ed.; Springer Verlag: Berlin, 1986, p 132.
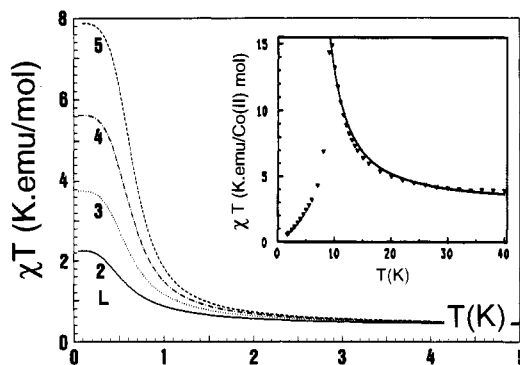
Figure 9. Theoretical behavior of triangular units of increasing size, from numerical treatment. The number of spins involved is related to L (number of rows) through $N_S = (L + 1)(L + 2)/2$. The best fit for Co$_2$(NO$_3$)(OH)$_3$ is given in the inset.

$1)(L + 2)$, so that the computations were limited to 21 spins. The results for a series of increasing size show a slow convergence towards the solution of the infinite system. The variation of the χT product as function of $kT/\lvert J\rvert$ for some triangular units, with size ranging from 6 to 21 spins, is illustrated in Figure 9. It is to be noted that taking into account finite size effects through scaling theory allows an improvement of the description of the infinite system.[30] As shown in Figure 9, by using the results computed for a 21 spin unit, we obtained a good agreement between theory and experiment (Figure 9). The parameters, listed in Table I, differ somewhat from those given by HTS analysis. The discrepancy is probably due to the size effect in the numerical analysis. In turn, the consideration of interlayer interactions (j) through molecular field approximation, confirms the 2D character of Co$_2$(NO$_3$)(OH)$_3$ ($\lvert j\rvert$ is less than 10^{-2} K), while unambiguous values of J and j are difficult to deduce for Co(OH)$_2$.

As emphasized above, the specific heat of magnetic origin is characterized by a λ-type anomaly at T_c and a broad peak reflecting strong spin correlations at higher temperatures. The analysis of the magnetic entropy reveals that only a few percent of the theoretical value $R \ln (2)$ is spent at the transition (41% for the hydroxide, 36% for the hydroxonitrate), confirming that short range order still remains far above T_c. Note that for 3D systems, less than 25% of the entropy change occurs above T_c.

Before the experimental specific heat is discussed, it is worth recalling that the 2D Ising model is the only one which presents a "conventional" long range order transition.[31] The 2D transition temperature is only slightly modified by the effect of small interlayer interactions.[1] The situation differs for the Heisenberg[32] and XY[33] two-dimensional magnetic systems for which no long-range order is predicted at finite temperature. However, for the latter, Kosterlitz and Thouless[34] have shown that a divergence of the in-plane correlation length occurs at non zero temperature (T_{KT}) with a singularity of specific heat (finite peak) for T slightly higher than T_{KT}. In the case of the 2D Heisenberg model, only a Schottky-type anomaly, similar to that of the chain model is obtained. From these theoretical predictions and the magnetic contributions to the entropy and specific heat, the following points may be made. (i) In agreement with susceptibility results, magnetic in-plane correlations are clearly evidenced. For pure Ising systems, only a sharp peak is predicted at the phase transition, while the experimental data exhibit a second anomaly around 25–30 K. In fact, the observed bumps may be due to a poor determination of the lattice contributions in this temperature region. (ii) XY-type anisotropy could explain the broader peak

(30) Fernandes, J. B. A.; Brady Moreira, F. G. *Physica A* **1990**, *170*, 43.
(31) Onsager, L. *Phys. Rev.* **1944**, *65*, 117.
(32) Mermin, N. D.; Wagner, H. *Phys. Rev. Lett.* **1966**, *17*, 1133.
(33) Stanley, H. E. *Phys. Rev.* **1968**, *20*, 589.
(34) Kosterlitz, J. M.; Thouless, D. J. *J. Phys.* **1973**, *C6*, 1181.

of C_{mag} for $Co(OH)_2$, since as mentioned above, the trigonal symmetry of cobalt(II) layers may induce planar anisotropy. In fact, particle size effect may also explain the shape of the peak, as demonstrated by Onsager[31] and Domb[35] on basis of the 2D Ising model, and experimentally by Soraï[4] for $Ni(OH)_2$. Indeed, it was shown that the peak of specific heat decreases and becomes less sharpened when particle size diminishes. (iii) the variation of C_{mag} for $Co_2(NO_3)(OH)_3$, in the vicinity of the phase transition, obeys the standard relation $C_{mag} = A[T_c - T)/T_c]^{-\alpha} + B$, with $\alpha = -0.37$ (Figure 6). The critical exponent α differs from standard values expected for Ising (namely 0.110), XY (-0.008), or Heisenberg (-0.116) models but, if the previous findings from Monte Carlo simulations are referred to,[36] it appears that layered triangular arrays may entail unusual power law variations.

Finally, it can be outlined that low-temperature specific heats ($T < T_c$) show a AT^2 dependence, with $A = 25 \pm 2$ mJ/(K^3 mol) for $Co(OH)_2$ and $A = 46 \pm 2$ mJ/(K^3 mol) for $Co_2(NO_3)(OH)_3$, which agrees with the existence of 2D spin-waves with a linear relation dispersion. Such a result is in contradiction with the Ising model used above (logarithmic divergence of C_{mag}), but the result is predicted by the XY triangular model.

V. Concluding Remarks

All these results demonstrate the low dimensional character of the title compounds with ferromagnetic in-plane interactions. The presence of nitrate groups in $Co_2(NO_3)(OH)_3$ may explain the difference between J values, although the average distances and bond angles are very similar.

Both compounds thus exhibit a long-range ordering at close temperatures, although the interlayer distances differ significantly. On basis of the molecular field approximation, it is shown that the 3D ordering temperature is given by $kT_c = \xi^2 jS^2$ where ξ is the in-plane correlation length at the transition. It thus appears that T_c is mainly driven by the divergence of ξ upon cooling down to zero or T_c^{2D}, depending on the spin anisotropy. Owing to the

T_c values observed for the title compounds, this implies that in-plane correlations are strongly anisotropic (Ising or XY-like).

Magnetic findings indicate that the anisotropy is likely different at high and low temperatures, in particular in the case of Co_2-$(NO_3)(OH)_3$. This can be explained from structural arguments; the Co(II) layer obeys the trigonal symmetry in the case of $Co(OH)_2$ but, due to the presence of bridging (NO_3) groups, the symmetry is lowered in $Co_2(NO_3)(OH)_3$. In our case, the rhombic distortion, favoring an ordering of the spins in layers, may be responsible of the Ising-like anisotropy of the spins within the XY plane as the temperature is lowered. Nevertheless, even if the Ising model agrees with our results, some points remain to be clarified. (i) Using the relationship between J and T_c available for a pure Ising layer, and the J values deduced from the above analysis, we obtain T_c = 8.4 and 6.7 K for $Co(OH_2)$ and Co_2-$(NO_3)(OH)_3$, respectively, which slightly differ from the observed values. (ii) The low-temperature specific heat agrees well with the XY model. However, the lack of theoretical calculation for the quantum XY approach does not allow to check its validity with respect to the Ising model.

Obviously, further experiments such as inelastic neutron scattering are needed to draw definite conclusions. Experiments which involve replacing Co(II) by the isotropic ion Mn(II) or the anisotropic one Ni(II) are in progress for a better understanding of these planar systems.

Appendix 1.

High-temperature series coefficients of the magnetic susceptibility for the $S = ^1/_2$ Ising triangular lattice are as follows.[27]

$a_1 = 2$	$a_6 = 2.446\ 614\ 583\ 333\ 30$
$a_2 = 1.875$	$a_7 = 2.001\ 082\ 633\ 574\ 30$
$a_3 = 2.125$	$a_8 = 2.450\ 978\ 015\ 718\ 00$
$a_4 = 2.289\ 062\ 5$	$a_9 = 2.415\ 486\ 185\ 386\ 70$
$a_5 = 2.391\ 403\ 982\ 426\ 30$	$a_{10} = 2.362\ 489\ 250\ 223\ 50$

Supplementary Material Available: Figures showing the X-ray diffraction pattern $Co_2(OH)_3(NO_3)$, infrared spectra for $Co(OH)_2$ and Co_2-$(NO_3)(OH)_3$, and ATG-ATD curves obtained for $Co(OH)_2$ and $Co_2(NO_3)(OH)_3$ under air (4 pages). Ordering information is given on any current masthead page.

(35) Domb, C. *Proc. Phys. Soc.* **1965,** *86,* 933.
(36) Kawamura, H. *J. Phys. Soc. Jpn.* **1989,** *58,* 2, 584.