

Contribution from the Groupe des Matériaux Inorganiques, IPCMS, EHICS, 1 Rue Blaise Pascal, 67008 Strasbourg, France, and Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bl. 11, 1040 Sofia, Bulgaria

## Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O: A Novel Double-Chain Compound with Competing Interactions

S. Angelov,<sup>1a</sup> M. Drillon,<sup>\*1b</sup> E. Zhecheva,<sup>1a</sup> R. Stoyanova,<sup>1a</sup> M. Belaiche,<sup>1b</sup> A. Derory,<sup>1b</sup> and A. Herr<sup>1b</sup>

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Magnetic susceptibility and magnetization measurements of the newly synthesized cobalt(II) hydroxide nitrate Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O show that this system presents above 2.5 K a low-dimensional magnetic behavior. It is described in terms of Ising-like  $S = 1/2$  double chains with two nearest-neighbor exchange interactions,  $J_1 = 22.8$  K and  $J_2 = -9.75$  K. The couplings between cobalt(II) ions are discussed using structural data for the in-chain and interchain exchange pathways. A weak coupling between double chains ( $J' \approx 0.2$  K) leads to an antiferromagnetic ordering below 2.5 K which undergoes a metamagnetic transition in relatively low magnetic field.

### Introduction

The study of compounds with low-dimensional magnetic networks usually permits a rigorous determination of the exchange interactions between neighboring metal ions and their correlation to the structure. Recent reports on some chain and layered cobalt(II) compounds (see for example refs 2 and 3 and the references therein) show that, at low temperature, these magnetic systems behave as collections of Ising  $S = 1/2$  effective spins coupled usually by ferromagnetic interactions. Nonmetallic compounds with predominant ferromagnetic interactions are in the focus of the nowadays materials research for two main reasons. The first one is purely fundamental and is, in fact, the challenge to escape the natural chemical-bond tendency of neighboring localized spins to acquire antiparallel orientation. The second one is related to the practical need for new molecular ferromagnetic materials. From both points of view, it is worthwhile to look for new systems which may lead to more insight into the relevant mechanisms. In the present paper, we investigate a novel cobalt(II) compound in which the metal ions are ordered in double chains with competing exchange interactions. The aim is to check both the applicability of one-dimensional statistical models to describe the thermodynamic properties and the conditions for stabilizing a ferromagnetic material.

### Experimental Section

**Preparation of the Samples.** The cobalt hydroxide nitrate compound was prepared by adding an equivalent quantity of solid Li<sub>2</sub>CO<sub>3</sub> to a 75% solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Co:Li = 1:1) at 25 °C, an intensive stirring being performed. Then, the water was evaporated from the mixture at 100 °C up to obtaining a dry residue of the new cobalt hydroxide nitrate having a nice pink color. The accompanying solid LiNO<sub>3</sub> was eliminated by washing with acetone.

**Characterization of the Samples.** The Co(II) and NO<sub>3</sub> contents were determined complexometrically and by the Dewarda method,<sup>4</sup> respectively. The phase identification was made by means of a Siemens X-ray diffractometer, using Co K $\alpha$  radiation. Magnetic susceptibility and magnetization data were recorded from powder samples using Faraday-type fully automated magnetic equipment (Manics) in the range 4–300 K and a SQUID magnetometer (Métrologique) in the range 2–20 K. Some preliminary specific heat measurements were also carried out using a quasi-adiabatic method.<sup>5</sup>

### Results and Discussion

The X-ray diffraction pattern of the cobalt(II) hydroxide nitrate exhibits the same features (see the supplementary material) as

those of Ni(OH)(NO<sub>3</sub>)·H<sub>2</sub>O<sup>6</sup> and Zn(OH)(NO<sub>3</sub>)·H<sub>2</sub>O.<sup>7</sup> It agrees with monoclinic symmetry, space group  $P2_1/c$ , and unit cell parameters  $a = 17.854$  Å,  $b = 3.226$  Å,  $c = 14.273$  Å, and  $\beta = 114.39^\circ$ .

The structure, shown in Figure 1, may be described as infinite double chains of edge-sharing octahedra Co(OH)<sub>3/3</sub>(NO<sub>3</sub>)<sub>1/1</sub>·(H<sub>2</sub>O)<sub>2/2</sub> running along the  $b$  axis. Two distinct orientations of the double chains exist in the plane perpendicular to the  $b$  axis. Each cobalt atom is coordinated to three hydroxyl ions, two water molecules, and one oxygen atom belonging to a nitrate group. Within elementary chains, the cobalt(II) octahedra are linked by one oxygen (of a water molecule) and one hydroxyl ion, while these chains are connected to each other through hydroxyl ions, only. Finally, nitrate groups are linked to the outer unshared corners and thus maintain the packing of twin chains through hydrogen bonds with water molecules.

The nearest-neighbor cobalt(II) distance between adjacent double chains is 6.89 Å (determined from unit cell parameters and atomic positions for the zinc derivative). In turn, the shortest Co–Co distances within a double chain are found to be 3.23 Å along the  $b$  axis and 3.05 Å in the other direction.

Chemical analysis is in good agreement with the formula Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O. Metal impurities which could be at the origin of the magnetic findings discussed hereafter are not detected.

The temperature dependence of the  $\chi_M T$  product is plotted in Figure 2, for a static applied field  $H = 1$  T.  $\chi_M T$  is nearly constant between 150 and 300 K, witnessing a rather pure Curie-like behavior with a Curie constant close to 3.5 emu·K·mol<sup>-1</sup>. This value corresponds to an effective magnetic moment of 5.3  $\mu_B$  per Co(II) ion. Below 150 K,  $\chi_M T$  decreases, exhibiting a minimum around 30 K and a strong increase on further cooling. A similar variation was already reported for different 1d ferrimagnets with either two different spin sublattices or an exotic stacking of the metal ions.<sup>8</sup> In fact, we will show below that the origin of such a behavior is, in this case, rather different. The value of 5.3  $\mu_B$  is typical for high-spin octahedral Co(II) complexes.<sup>9</sup> For such species, the <sup>4</sup>T<sub>1g</sub> ground triplet splits under the combined action of spin-orbit coupling and noncubic crystal-field terms, giving six Kramers doublets with an effective nonisotropic  $S = 1/2$  ground state. The cooling depopulates the higher doublets with respect to the low-lying one, resulting in gradual decrease of the effective magnetic moment below 150 K. The increase of  $\chi_M T$  below 30 K is the signature of ferromagnetic exchange interactions between the effective  $1/2$  spins of adjacent Co(II) ions.

The temperature dependence of the magnetic susceptibility is shown, for different external magnetic fields, in Figure 3. Below 15 K, the susceptibility depends on the external field, indicating the presence of large fluctuations of the resulting magnetic moment. Nevertheless, the long-range (3d) magnetic ordering is only observed below 2.5 K.

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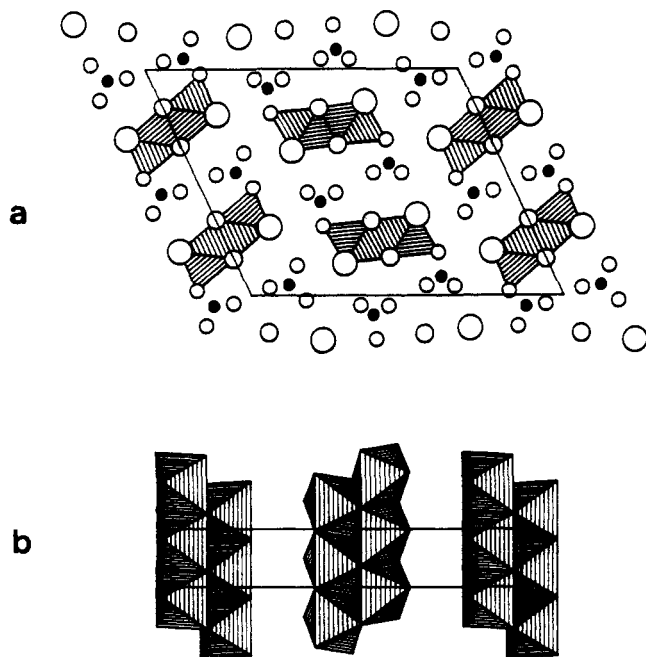


Figure 1. Structure of Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O, showing the isolated double chains of cobalt(II) octahedra (a) in the (a, c) plane and (b) in the perpendicular direction.

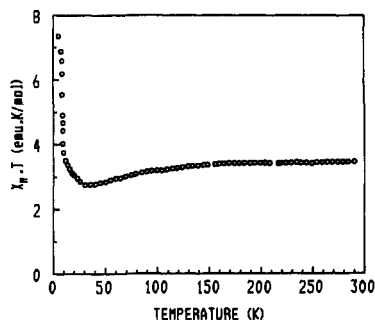


Figure 2. Temperature dependence of the  $\chi_M T$  product. ( $\chi_M$  is the molar magnetic susceptibility of Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O).

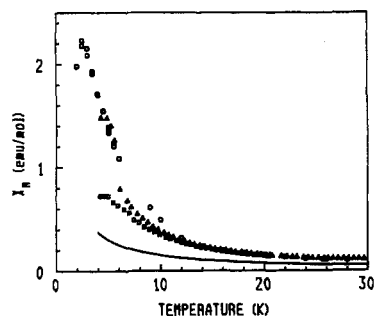


Figure 3. Susceptibility of Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O vs  $T$  between 4 and 30 K in different static magnetic fields: 14000 Oe (○); 2030 Oe (▲); 33 Oe (□). The dotted line is the Curie law for  $g = 4$  and  $S = 1/2$ .

The field dependence of the magnetization is displayed in Figure 4 at three characteristic temperatures: 12, 5, and 2 K. At 12 and 5 K (i.e. when the susceptibility is field dependent, but there is not yet long-range ordering), the magnetization becomes non-linear in relatively low fields. The behavior is typical for spins strongly coupled by ferromagnetic exchange interactions. However, due to the low dimensionality of the magnetic network (double chains of  $1/2$  spins), this interaction cannot induce a 3d magnetic ordering. Below the maximum in the  $\chi_M(T)$  curve, the magnetization varies linearly with the field up to ca. 700 Oe where a clear transition to a paramagnetic state takes place (Figure 4). Such a behavior, co-called metamagnetism, is also rather typical for different cobalt(II) compounds.<sup>3,10</sup> The metamagnetic be-

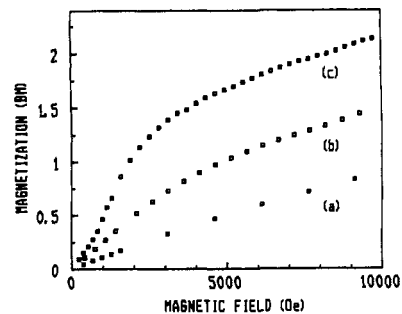


Figure 4. Magnetization of Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O versus magnetic field at different temperatures: (a) 12 K; (b) 5 K; (c) 2 K.

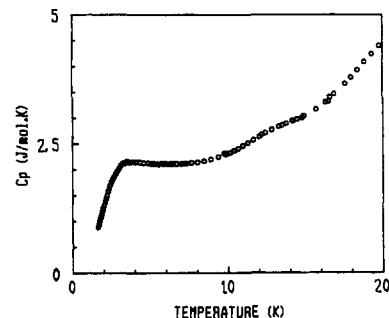


Figure 5. Specific heat of Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O (J/(mol·K)) vs temperature.

havior below 2.5 K confirms the hypothesis that the  $\chi_M(T)$  maximum corresponds to the occurrence of a 3d-antiferromagnetic ordering. The same conclusion can be drawn when inspecting the temperature dependence of the specific heat (Figure 5). The maximum at 3 K agrees well with the  $\chi_M(T)$  maximum (2.5 K), while the bump at 12.5 K has to be related to the short-range correlations in the  $S = 1/2$  double chains.

An estimation of the low-dimensional character of the title compound can be made from the effective ratio between interchain ( $J'$ ) and in-chain ( $J$ ) exchange interactions. Richards' formula allows one to relate these exchange constants to the 3d-transition temperature:<sup>11</sup>

$$T_c = CS(S + 1)JJ'T^{1/2} \quad (1)$$

In our case, the interchain coupling is responsible for the anti-ferromagnetic ordering between the giant magnetic moments of neighboring chains. It may roughly be estimated from the critical value of the field at which the system undergoes a metamagnetic transition (see Figure 4). By assuming  $J' \approx H_c$ , for  $H_c = 700$  Oe and  $g = 4$ , we get  $J' \approx 0.2$  K. Using the above formula, one obtains  $J \approx 5$  K (the exchange Hamiltonian is written  $H_{ex} = -2J \sum_i S_i S_{i+1}$ ). It is to be noted that close values were obtained for other cobalt(II) one-dimensional ferromagnets, as for instance ((CH<sub>3</sub>)<sub>3</sub>NH)CoCl<sub>3</sub>·2H<sub>2</sub>O.<sup>3</sup> The ratio  $J'/J$  obtained is about  $10^{-2}$ , confirming that the double chains are rather well-isolated magnetically in a large-temperature scale. Owing to these findings, a theoretical model based on isolated double chains of cobalt(II) ions is reported hereunder for describing the magnetic behavior.

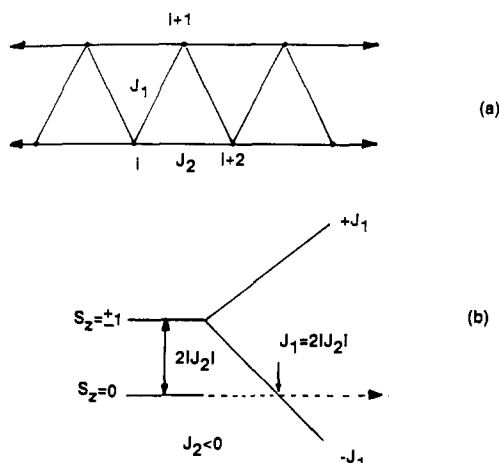
#### Analysis of the Results

Consider the infinite Ising-like double chain made of two interacting linear chains of  $1/2$  spins (Figure 6a). Each magnetic moment is linked to an even number of neighbors by two different exchange interactions,  $J_1$  between elementary chains (zigzag pathway) and  $J_2$  in the chain direction. The corresponding Hamiltonian may be written as

$$H = -\sum_i 2J_1 S_i S_{i+1} + 2J_2 S_i S_{i+2} \quad (2)$$

where the  $S_i$ 's stand for the z-component of spin operators, in

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**Figure 6.** (a) Double (triangular) chain (railroad trestle lattice) and (b) energy level scheme for the renormalized Hamiltonian. (See the text, eq 5).

agreement with the symmetry of the Co(II) ground state. This corresponds to the Ising chain with next-nearest-neighbor interactions, the treatment of which has been discussed by Montroll.<sup>12</sup>

It is readily shown that this problem can be solved exactly by the transfer matrix technique.<sup>13</sup> For zero-magnetic field, the transfer matrix reduces to two  $2 \times 2$  diagonal blocks, thus allowing for analytical expression of the partition function:

$$Z(0) = b \cosh K_1 + b^{-1} + [b^2 \sinh^2 K_1 + 2 \cosh K_1 + 2]^{1/2} \quad (3)$$

where  $K_1 = J_1/2kT$ ,  $K_2 = J_2/2kT$ , and  $b = \exp(K_2)$ . In turn, for nonzero magnetic field, the partition function cannot be expressed in a simple form, but it appears that the secular polynomial is an even function with respect to  $H$ . We then deduce a somewhat cumbersome expression for the magnetic susceptibility:

$$\chi_M = (Ng^2\mu_B^2/8kT) \times [Z(0)^2 ab + 2(1 - a^2)Z(0) + a^3 b^{-1} + a^{-1} b^{-1} - 2ab^{-1}]/ER \quad (4)$$

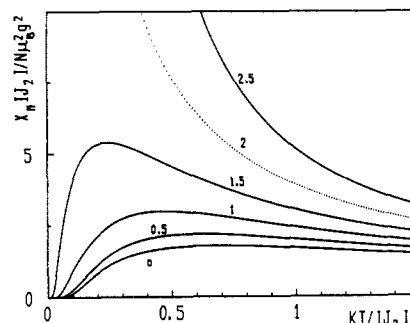
where  $a = \exp(K_1)$ ,  $E = a^{-2} - \cosh K_2 + a^{-1}R$ , and  $R = [a^2 \sinh^2 K_2 + 2 \cosh K_2 + 2]^{1/2}$ . Note that this expression refers to a two-spin unit. For  $J_1$  or  $J_2$  equal to zero, it merely reduces to the magnetic susceptibility of the regular  $S = 1/2$  Ising chain derived by Fisher.<sup>14</sup>

Obviously, several situations may be encountered depending on the respective values of the  $J_1$  and  $J_2$  parameters. For positive (ferromagnetic)  $J_2$ , the discussion is rather easy. Each elementary chain behaves as a ferromagnetic species whose resulting moment is parallel or antiparallel to that of the neighboring one, depending on the sign of  $J_1$ ; accordingly, the ground state is ferromagnetic ( $J_1 > 0$ ) or antiferromagnetic ( $J_1 < 0$ ).

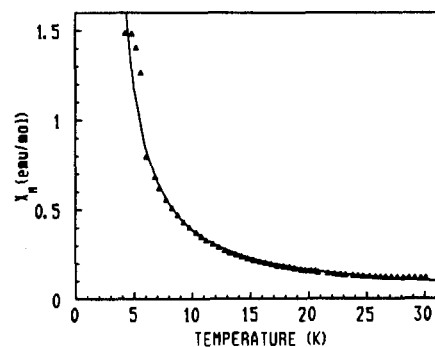
Let us focus now on the case  $J_2 < 0$  (antiferromagnetic), for which frustration effects occur whatever the sign of  $J_1$ . For more insight, we can renormalize the Hamiltonian (2) writing it in the following way:

$$H = -\frac{1}{2} \sum_i J_1 T_i + J_2 T_i T_{i+1} \quad (5)$$

Here  $T_i$  stands for the scalar product  $S_i S_{i+1}$ . The initial double chain is then transformed into a linear one, in which  $J_2$  couples Ising spins ( $T = \pm 1$ ) and  $1/2 J_1$  is equivalent to an "external" field. As noted in Figure 6, there is, for  $J_1 = 2IJ_2$ , a full compensation between both exchange interactions leading to a degenerate ground state. The chain behaves like a collection of magnetically isolated  $1/2$  spins, and the magnetic susceptibility obeys the Curie law (dotted curve in Figure 7). The situation may be described as a perfectly frustrated one.



**Figure 7.** Scaled magnetic susceptibility ( $\chi_M IJ_2 I / N \mu_B^2 g^2$ ) vs reduced temperature ( $kT/IJ_2 I$ ) for different  $J_1/IJ_2 I$  ratios ( $J_1 > 0$ ).



**Figure 8.** Comparison of the experimental and theoretical magnetic susceptibility in nearly zero magnetic field using eq 5.

When  $IJ_1 I > 2IJ_2 I$ , the ground state is ferromagnetic or antiferromagnetic according to the sign of  $J_1$ . Conversely, for weak  $IJ_1 I$  values ( $IJ_1 I < 2IJ_2 I$ ) each elementary chain is antiferromagnetic and the double chain behaves as a simple 1d antiferromagnet. Then the decrease of  $\chi_M T$  at low temperature is well described by  $\exp((2J_2 + IJ_1 I)/2kT)$ . Magnetic susceptibility vs temperature plots are given in Figure 7 for different  $J_1/IJ_2 I$  ratios ( $J_1 > 0$ ).

Assuming that this model holds in the range 3–30 K, where only the lowest Kramers doublet of Co(II) is populated, we have fitted the experimental susceptibility with the formula derived above (Figure 8). The best agreement between theory and experiment is obtained for  $J_1 = 22.8$  K,  $J_2 = -9.75$  K, and  $g = 3.83$ , corresponding to ferromagnetic interchain couplings and antiferromagnetic in-chain ones; note that the Landé factor is not far from the expected value  $g = 4$  for the Co(II) ion. Attempts to promote other sets of ( $J_1$ ,  $J_2$ ,  $g$ ) parameters in the fitting procedure were unsuccessful.

According to the model described above, we may deduce the value of  $J_{\text{eff}} = J_1 - 2IJ_2 I = 3.3$  K, which agrees well with the estimated one using the 3d ordering temperature and the critical field for the metamagnetic transition (eq 1).

Let us discuss now the values of the in-chain and interchain exchange constants in relation with structural findings. First, it appears that  $J_1$  and  $J_2$  have opposite signs although the connections between cobalt(II) polyhedra are similar in both directions (edge-sharing octahedra). In fact, a closer examination of the structure shows that the bibriges within and between elementary chains are different; they involve two hydroxyl groups for the latter (type I), a water molecule and an hydroxyl group for the former (type II). It follows that the structural features are expected to differ for both types of connections. The relevant bond lengths and bond angles within equatorial plane of edge-sharing octahedra, computed from structural parameters and atomic positions of the zinc derivative, are given in Figure 9. The presence of one hydroxyl bridge for the type II pathway (interaction  $J_2$ ) promotes an increase of the related Co(II)–O–Co(II) angle up to  $101.75^\circ$ . Further, we note the large Co(II)–O(H<sub>2</sub>) bond length of 2.591 Å, which inhibits the exchange coupling through the water molecule. Accordingly, only the hydroxyl group should participate to the exchange coupling between singly occupied  $d_{x^2-y^2}$  (site I

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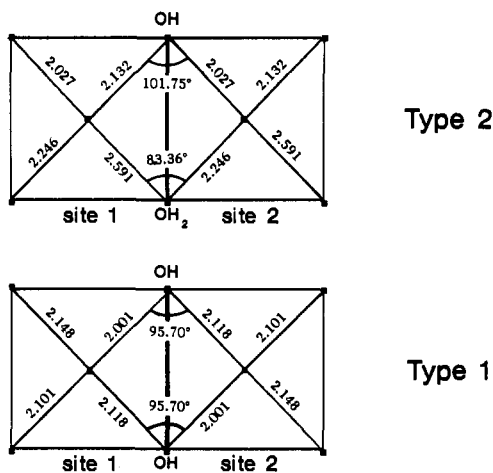


Figure 9. In-chain (type II) and interchain (type I) connections between cobalt(II) polyhedra showing the relevant bond lengths and bond angles.

or 2) and  $d_{z^2}$  (site 2 or 1) magnetic orbitals; such a coupling is expected to be antiferromagnetic.

Conversely, symmetrical pathways through hydroxyl bridges are observed for the type I connection (interaction  $J_1$ ). Owing to the equatorial bond lengths, the in-plane  $d_{x^2-y^2}$  magnetic orbitals overlap through oxygen  $p_\sigma$  orbitals with a bridging angle of ca. 95.7°. On the basis of experimental works on the hydroxo-bridged copper(II) complexes, which involve the same  $d_{x^2-y^2}$  magnetic orbital, a strong ferromagnetic coupling is predicted for such a bridging angle, due to accidental orthogonality of the magnetic orbitals.<sup>15</sup> For instance, [Cu(pby)OH]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> exhibits an exchange interaction of +248 K for a bridge angle of ca. 95.6°,<sup>16</sup> while the interaction drops to -252 K for [Cu(2miz)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> in which the bridge angle is 99.4°.<sup>17</sup> In Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O, the exchange interaction involves in fact further contributions to  $J_1$ , since three unpaired electrons participate to the exchange process. Thus, an antiferromagnetic contribution should result

from the direct overlap between  $d_{xy}$  orbitals, but this one does not compensate the strong ferromagnetic coupling discussed above.

On the other hand, it can be noticed that the exchange interaction depends also on the metal-metal distance, which is 3.23 Å within elementary chains and 3.05 Å between neighboring chains. It is well documented that small increase in the bond length induces a large decrease in the magnitude of the exchange coupling, according to the empirical Bloch law  $J \approx d^{-10}$ .<sup>18</sup> In fact, the exchange mechanisms responsible for the  $J_1$  and  $J_2$  interactions differ, as emphasized above, so that such a correlation is questionable in the present context.

### Conclusions

The title compound Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O is the first genuine realization of a low-dimensional magnetic system made of quasi-isolated double chains of Ising  $1/2$  spins. Because of the sign of the in-chain and interchain interactions, the spins in the double chain are subjected to competing effects. This is visualized in terms of an effective linear chain of ( $\pm 1$ ) Ising spins coupled antiferromagnetically by  $J_2$  and experiencing an effective "magnetic" field,  $1/2 J_1$ . The positive value of  $J_1$ , related to the coupling along the zigzag pathway, results likely from the accidental orthogonality of the  $d_{x^2-y^2}$  magnetic orbitals, in agreement with previous findings on hydroxo-bridged copper(II) complexes. This coupling forces the spins to be parallel, although in-chain interactions are antiferromagnetic, thus stabilizing a ferromagnetic ground state.

Finally, it can be emphasized that such a 1d system with competing interactions may be of considerable interest for studying spin glass and random field problems. The investigation of a frustrated 2d lattice built up by bringing together the cobalt(II) double chains is in progress.

**Acknowledgment.** We are indebted to Drs. Kostadin Petrov (Sofia) and Boissier (Strasbourg) for the X-ray diffraction measurements. Dr. Kuentzler (Strasbourg) is kindly acknowledged for the preliminary specific heat measurements. S. Angelov is extremely indebted for a one school year tenure in EHICS (Strasbourg).

**Supplementary Material Available:** A table of the X-ray diffraction data (interplane distances and relative intensities) for Co(OH)(NO<sub>3</sub>)·H<sub>2</sub>O (1 page). Ordering information is given on any current masthead page.

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