An original 1D Cu–Co heterometallic compound: synthesis, structure and magnetic properties

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A novel heterobimetallic system, $^{1}{}_{\infty}[\mathrm{LCu^{II}Co^{II}(NCS)_2}]$ (**1**), was obtained by reacting the neutral mononuclear complex [LCu] with cobalt(II) acetate in the presence of potassium thiocyanate (L is the dianion of the Schiff base resulting from the 2 : 1 condensation of 3-methoxysalicylaldehyde with 1,3-propanediamine). The crystallographic investigation of **1** reveals a one-dimensional alternating zig-zag chain-like structure, made of dinuclear {LCuCo} units linked by thiocyanate bridges. The copper(II) ion is pentacoordinate to the N_2O_2 donor set of the Schiff base ligand in the basal plane, with the apical position occupied by the sulfur atom. The cobalt ion displays a strongly distorted (4 + 2) octahedral geometry. The distance between the phenoxo-bridged metal ions is 3.149(1) Å. The Cu···Co distance for the NCS^- bridged ions is equal to 6.125(1) Å. The magnetic properties of **1** were investigated in the temperature range 2–300 K and they are explained by a strong antiferromagnetic Cu(II)–Co(II) exchange interaction through the phenoxo bridges and a weak ferromagnetic Cu(II)–Co(II) interaction through the thiocyanato bridges. Several theoretical models are proposed to fit the magnetic data of **1**, the most appropriate one being the full matrix diagonalization for a closed-chain of four dinuclear units $[\mathrm{Cu^{II}Co^{II}}]$, taking into account two different exchange parameters and a D term, which yielded the following results: $J = -101.2\ \mathrm{cm^{-1}}$, $j = 2.8\ \mathrm{cm^{-1}}$, $D = -0.11\ \mathrm{cm^{-1}}$, $g = 2.38$.

Introduction

The magnetism of one-dimensional systems is a field which has been widely investigated.[1] The studied compounds are either homometallic or bimetallic. If the magnetic centres have the same nature and are equally spaced the chain is said to be regular[2] and its magnetic properties depend on one exchange coupling constant. Otherwise we face an alternating chain which generally supports two intrachain exchange parameters.[3–5] The antiferromagnetic alternating (J_i and J_{i+1}) systems have received particular attention, which contrasts with the paucity of data related to alternating chains with coupling constants (J_i and J_{i+1}) of different signs. Furthermore the most mentioned examples involve $S = \frac{1}{2}$ centres. A few systems with $S > \frac{1}{2}$ have been reported and reviewed.[6] They consist of alternate chains of nickel(II) or manganese(II) ions with azido bridges. As an example of their behaviour, the related $\chi_M T$ product (χ_M being the molecular susceptibility reported for a dinuclear entity) for a manganese chain[7] decreases continuously upon cooling down to 2 K. This behaviour contrasts with the characteristic minimum observed in the $\chi_M T$ *vs.* T curves of the alternating antiferromagnetic chains.[8] A satisfying description of the magnetic properties of the manganese chain has been gained from a theoretical model involving two exchange coupling constants.[7] At low temperature interchain interactions, which are mainly antiferromagnetic, have to be taken into account.

In the present paper we wish to set out a bimetallic (Cu, Co) alternating chain, **1**, with a magnetic behaviour different from the two aforementioned ones. The $\chi_M T$ values decrease upon lowering the temperature but not continuously, for the related $\chi_M T$ *vs.* T curve displays a pseudo-plateau around 40 K. The results of the structural study are also reported.

Results and discussion

Preparation of 1

The first observation of $^{1}{}_{\infty}[\mathrm{LCu^{II}Co^{II}(NCS)_2}]$ (**1**) was completely fortuitous when we attempted to obtain a new 3d–3d′–4f heterospin system by adapting a synthetic path we had already successfully used.[9,10] The synthetic strategy was based on a self-assembly process involving 3d–4f heterobinuclear cationic complexes and hexacyanometallate ions, $[\mathrm{M(CN)_6}]^{3-}$ [M(III) = Cr, Fe, Co]. Aiming to diversify the structural type, as well as the magnetic properties, of the expected heterotrimetallic species, we employed another anionic building-block, namely the tetraisothiocyanato cobaltate(II) ion, $[\mathrm{Co(NCS)_4}]^{2-}$. The reaction between $[\mathrm{LCuGd(NO_3)_3}]$ [L^{2-}: *N*,*N*-propylenedi

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(3-methoxysalicylideneiminato] and $(Et_4N)_2[Co(NCS)_4]$ led to the isolation of a highly crystalline product, whose crystallographic investigation reveals the formation of a novel [CuCo] complex, $^{1}{}_{\infty}[LCu^{II}Co^{II}(NCS)_2]$ (**1**).

Compound **1** can be obtained in a rational way as follows: the first step consists of the reaction of 3-methoxysalicylaldehyde and 1,3-diaminopropane (2 : 1 molar ratio) in methanol, followed by addition of copper acetate which yields the "compartmental complex ligand" [LCu]. This complex possesses an outer O_2O_2 binding site which has been previously used to accommodate 4f ions.[11] Although this site seems too large to coordinate a 3d ion, the reaction of [LCu] with cobalt(II) acetate in presence of potassium thiocyanate yields a very well-defined product analysed as $[LCu^{II}Co^{II}(NCS)_2]$.[12] This result is less surprising if we remember that [(Salen)Cu] species are able to coordinate cobalt ions to give $(SalenCu)_2Co(ClO_4)_2$ complexes studied for their magnetic properties but for which no structural determination has been realized.[13] In our case, the use of coordinating ligands (NCS^- instead of ClO_4^-) and of methoxy groups on the L ligand gives entities with a 1/1 Cu/Co ratio, as confirmed by the FAB^+ spectra. The main signal with an *m*/*z* value of 520(100) presents an isotopic feature attributable to the $[LCuCo(NCS)]^+$ cation.

Structural study

The main point of the crystal structure is the presence of "alternating" and "zig-zag" chains running parallel to the *a* axis, made of dinuclear {LCuCo} units linked by thiocyanate bridges. Within each dinuclear {LCuCo} unit (Fig. 1) the copper and cobalt ions are bridged by two phenoxo oxygen atoms belonging to the ligand L, with a Cu–Co separation equal to 3.149(1) Å. The copper ion completes its coordination sphere with the two imine nitrogen atoms from L. The four atoms of the N_2O_2 chromophore are almost planar since they are alternately displaced from the mean plane by less than 0.03 Å. The copper ion is pulled out of the equatorial plane by 0.139(2) Å toward the sulfur atom of the bridging thiocyanate which is linked by its nitrogen atom to the cobalt ion of a neighbouring {LCuCo} unit, so that the copper ion is pentacoordinate and adopts a slightly distorted square pyramid geometry. The bond lengths to Cu(II) are within the usual range observed for copper coordinated to Schiff bases (from 1.952(3) to 1.957(3) Å for Cu–O and from 1.970(4) to 1.972(4) Å for Cu–N bonds). The axial Cu–S bond length is larger, 2.766(2) Å.

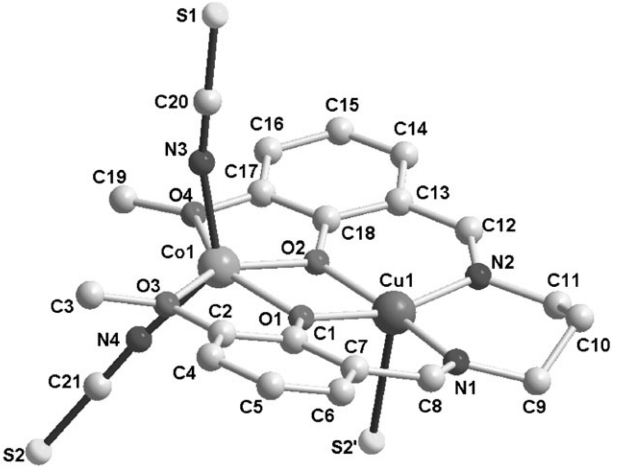

Fig. 1 Molecular structure of dinuclear $LCuCo(NCS)_2$ unit. Symmetry transformations used to generate equivalent atoms: (′) $x + 1/2$, y, $-z + 3/2$.

The cobalt coordination mode is more delicate to state precisely. At first sight, a tetrahedral environment comprising the two phenoxo oxygen atoms of the bridge and the two nitrogen atoms from the two coordinated thiocyanate ions can be envisaged. But the values of the Co–O (methoxy oxygen atoms) distances (2.438(4) and 2.484(4) Å) indicate that they are not large enough to discard the eventuality of Co–O bonds. In that case the hexacoordinate cobalt ion is in a strongly distorted (4 + 2) octahedral geometry. This observation will be confirmed later by the analysis of the magnetic properties.

Within the infinite $^{1}{}_{\infty}[LCu^{II}Co^{II}(NCS)_2]$ chains (Fig. 2), one of the two thiocyanate ligands participates in the bridging, the other one being only linked to the cobalt ion by its nitrogen atom. The Cu···Co distance for the NCS^- bridged ions is equal to 6.125(1) Å. Furthermore the {LCuCo} units have an up and down alternate disposition, which is clearly shown by the orientation of the three carbon atom diamino chain. This is due to the arrangement of the bridges of a particular {LCuCo} entity, NCS–Cu and Co–NCS, which are disposed on the same side of the {LCuCo} mean plane, alternately over and under. Two types of arrangements are present in the packing of the infinite chains in the crystal. For the chains related by a glide plane, the Co···Co, Cu···Cu and Co···Co distances are, respectively, equal to 11.961(1), 10.380(1) and 9.513(1) Å. For the centrosymmetrically related chains, these distances are equal to 7.370(1), 7.109(2) and 8.827(2) Å. From a magnetic point of view, we can consider that the chains are well isolated from each other.

Magnetic study

The structural study has confirmed that the {LCuCo} entities form alternating zig-zag chains in which two types of bridging units are operative: a double bridge involving the phenoxo oxygen atoms of the Schiff base ligand (Cu(O,O)Co) and a single one through the auxiliary NCS ligand (Cu–SCN–Co). The magnetic properties will depend on two parameters related to the Cu–Co exchange interactions supported by these two material links. The temperature dependence of the magnetic susceptibility in the 2–300 K range is shown in Fig. 3, in the $\chi_M T$ *vs.* T form, χ_M representing the magnetic susceptibility of an {LCuCo} unit. On lowering the temperature, $\chi_M T$ decreases continuously and reaches a pseudo-plateau around 50 K. As previously mentioned in the introduction, such behaviour has not yet been reported for a (Cu,Co) system. In the case of a ferrimagnetic behaviour, the $\chi_M T$ *vs.* T curve of a (Cu,Co) chain possesses a rounded minimum and increases at low temperature.[8] For an alternating chain, a $\chi_M T$ decrease is observed, without discontinuity.[7] These literature models cannot be used there for they are unable to fit the experimental results. Furthermore they do not take into account two coupling parameters between the $S = \frac{1}{2}$ ion and the spin of the $S > \frac{1}{2}$ ion, a possible spin–orbit coupling and a local anisotropy parameter.

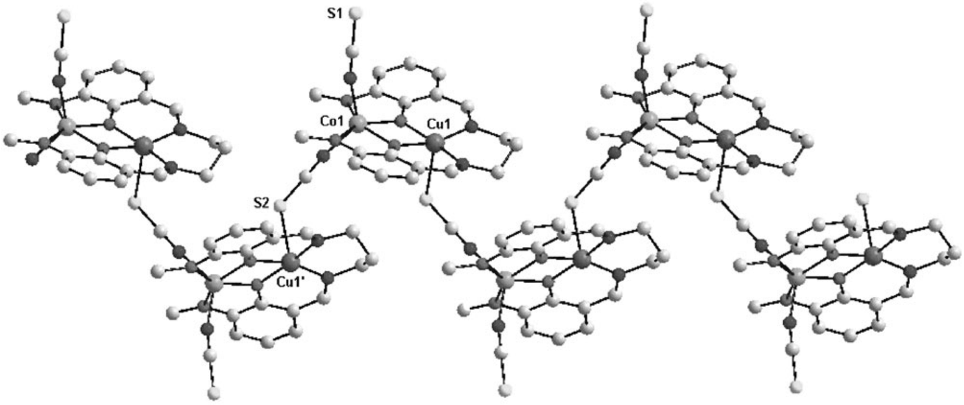

Fig. 2 1D coordination polymer $^{1}{}_{\infty}[LCu^{II}Co^{II}(NCS)_2]$ in the crystal structure **1**.

The shape of the $\chi_M T$ *vs.* T curve suggests an overall antiferromagnetic behaviour. At 300 K, the $\chi_M T$ value is equal to 2.25 cm^3 mol^{-1} K, and corresponds to the theoretical value calculated for two non interacting Cu(II) and Co(II) ions (2.25 cm^3 mol^{-1} K, assuming $g_{Cu} = g_{Co} = 2$). It decreases to 1.27 cm^3 mol^{-1} K at 50 K, gives a pseudo-plateau between 50 and 25 K and shows an abrupt decrease to 0.44 cm^3 mol^{-1} K at 2 K. The simplest way to analyse the magnetic behaviour is to consider the chain as an infinite sum of (Cu,Co) dimers with antiferromagnetic interactions established between the phenoxo bridged metal ions. Indeed, a look at the structure suggests that the main interaction is active within each dinuclear unit (Cu,Co) while the weaker interaction acts between the dinuclear units through the thiocyanate bridge, which justifies the first approximation. In that case, a simple isotropic spin Hamiltonian $\boldsymbol{H} = -\boldsymbol{J}\,(\boldsymbol{S}_{Cu}.\boldsymbol{S}_{Co})$ with the introduction of a Weiss term θ to account for other effects yields the following expression:

$$\chi_M T = \frac{N\beta^2 T}{3k(T-\theta)} \cdot g^2 \cdot \left[\frac{6 + 30\cdot\exp(2J/kT)}{3 + 5\cdot\exp(2J/kT)}\right]$$

The resulting parameters are $J = -106.6$ cm^{-1}, $\theta = -2.8$ K and $g = 2.32$. From the mean field approximation we can deduce a j parameter of -1.47 cm^{-1} if we consider that two neighbouring dimer units do interact. The agreement factor is quite good ($R = 1.0 \times 10^{-4}$). Here the term θ has no specific physical significance. We can conclude that, in addition to the main J intramolecular interaction, another interaction is at least necessary to reproduce the magnetic behaviour.

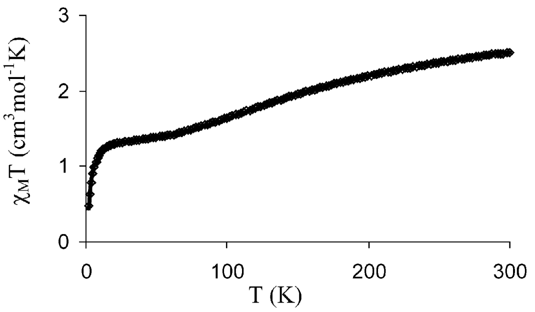

Fig. 3 Temperature dependence of $\chi_M T$ for **1**. The full line corresponds to the best data fit.

As the $\chi_M T$ decrease at low temperature could be due to the zero field splitting of the cobalt(II) ion ground state, the magnetic susceptibility has been computed by exact calculation of the energy levels associated with the spin Hamiltonian through diagonalization of the full matrix. Taking into consideration the zero field splitting and the main J interaction parameter within the dinuclear unit, we have not been able to fit in a correct way the low temperature part of the curve, even with large D values. This is not surprising if we remember that the orbital contribution is significantly quenched when the iron or cobalt environment[14,15] deviates from ideal octahedral geometry, as observed in our case.

In order to simplify the calculations for an infinite chain with two J interaction parameters, we have considered a tetranuclear complex with two J values but without a D term. In that case, a very nice fit is obtained over the entire 2–300 K temperature range with $J = -101.2$ cm^{-1}, $j = 2.4$ cm^{-1}, $g = 2.377$, $R = 7.0 \times 10^{-5}$. It is noteworthy that the calculated curve fits perfectly the pseudo-plateau around 50 K and the low temperature domain. It is clear that the large antiferromagnetic interaction J is attributed to the double bridge Cu(O,O)Co and the smaller term j to the Co–NCS–Cu link. At first sight, the existence of a ferromagnetic interaction is surprising but if we remember that the dinuclear (Cu,Co) entities are alternately disposed up and down, it becomes clear that the spins of the cobalt and copper ions located at the two ends of the NCS bridge are oriented in a parallel direction. Surprisingly the ferromagnetic j term induces a decrease of the $\chi_M T$ value for it gives an antiparallel arrangement of the larger cobalt spins. A more sophisticated model using exact diagonalization of a closed-chain of four dinuclear units and taking into account a D term yields a very similar result with $J = -101.2$ cm^{-1}, $j = 2.8$ cm^{-1}, $D = -0.11$ cm^{-1}, $g = 2.38$, $R = 7.0 \times 10^{-5}$. The later result provides clear evidence for the absence or very small contribution of zero field splitting in our chain compound. We can also remark that the four centres and the eight centres models give very similar results, probably as a consequence of the large difference in the two interaction parameters, J and j. A comparison between the later data and the data given by the first retained model is puzzling. If the main J factor is practically equal in the two models (-106.6 and -101.2 cm^{-1}), the lower parameter j is of opposite sign (-1.47 and 2.8 cm^{-1}). A closer look at these models gives a simple answer. In the model described first, the chain compound is considered as an infinite assembly of entities with an $S = 1$ resulting spin linked together by a weaker interaction which is necessarily antiferromagnetic as the $\chi_M T$ value decreases. In the later model, we have a finer tuning of the chain compound for we assign the lower j parameter to the thiocyanate anion bridging the cobalt ion of one dimer entity to the copper ion of the next one. As these dinuclear units are up and down disposed, it becomes clear that a ferromagnetic j interacting parameter is expected, as a consequence of the main intradinuclear and antiferromagnetic J parameter. It has to be noted that dinuclear copper(II) and 1D nickel(II) complexes[16] with end-to-end thiocyanate bridges have appeared in the literature and their magnetic studies have confirmed the presence of weak ferromagnetic interactions through these thiocyanate bridges, in good agreement with the present results. A weak ferromagnetic Cu(II)–Co(II) interaction was also found recently with a hexanuclear thiocyanato bridged complex.[17]

Conclusion

To sum up the present work, it may be noted that the crystallographic investigation demonstrates that the heterodinuclear {LCuCo} units are linked by thiocyanate bridges to give a one-dimensional alternating zig-zag chain-like structure in which the copper ions are pentacoordinate and the cobalt ions in a strongly distorted octahedral geometry. The magnetic study is very informative. Two Cu–Co magnetic interactions are active, the stronger one through a double bridge involving the phenoxo oxygen atoms of the Schiff base ligand (Cu(O,O)-Co) and the weaker one through the single auxiliary NCS ligand (Cu–SCN–Co). Whatever the theoretical model retained, the main interaction is antiferromagnetic and practically constant while the other interaction can be antiferromagnetic or ferromagnetic, depending on the model. The full matrix diagonalization for a closed-chain of four dinuclear units [$Cu^{II}Co^{II}$], taking into account two different exchange parameters and a D term, is the most appropriate model. It yields the following results: $J = -101.2$ cm^{-1}, $j = 2.8$ cm^{-1}, $D = -0.11$ cm^{-1}, $g = 2.38$. These results are corroborated by previously published data, which confirm the presence of weak ferromagnetic interactions in dinuclear copper(II) and 1D nickel(II) complexes with end-to-end thiocyanate bridges. The structural determination brings the final evidence for the {LCuCo} units having an up and down alternate disposition which is clearly shown by the orientation of the three carbon atom diamino chain of the Schiff base ligand L.

Experimental

Materials

1,3-Diaminopropane, *ortho*-vanillin, $Cu(Ac)_2 \cdot H_2O$, $Co(Ac)_2 \cdot 4H_2O$, KNCS (Aldrich) were used as purchased. High-grade solvents (acetonitrile, ethanol and methanol) were used for the syntheses of ligands and complexes. The LCu and $LCuGd(NO_3)_3$[11] complexes were prepared as previously described. For the synthesis of $(Et_4N)_2[Co(NCS)_4]$, we used a procedure already described in the literature.[18] The compound was obtained as a blue powder, by mixing the aqueous solutions of $CoCl_2 \cdot 6H_2O$ (0.47 g, 2×10^{-3} mol), $Et_4NCl \cdot H_2O$ (0.74 g, 4×10^{-3} mol) and KNCS (0.78 g, 8×10^{-3} mol) in a 1 : 2 : 4 molar ratio.

$^1_\infty[LCu^{II}Co^{II}(NCS)_2]$ (1). An acetonitrile solution of $(Et_4N)_2[Co(NCS)_4]$ (0.055 g, 1×10^{-4} mol) was poured into a solution of $LCuGd(NO_3)_3$ (0.074 g, 1×10^{-4} mol) in methanol/acetonitrile (1/1). Slow evaporation of the resulting turquoise-green solution yielded blue crystals that were filtered off, washed with methanol, diethyl ether and dried. Yield: 0.035 g (60%). Anal. Calcd for $C_{21}H_{20}CoCuN_4O_4S_2$: C, 43.6; H, 3.5; N, 9.7. Found: C, 43.5; H, 3.4; N, 9.4. Characteristic IR absorptions (KBr): 2088, 1616, 1476, 1297, 1253, 1227, 1073, 743 cm^{-1}.

The complex was obtained on a larger scale by addition of cobalt(II) acetate (0.12 g, 5×10^{-4} mol) and potassium thiocyanate (0.10 g, 1×10^{-3} mol) to a methanol suspension of [LCu] (0.20 g, 5×10^{-4} mol). After stirring for 1 h, the resulting precipitate was filtered off, washed with methanol, diethyl ether and dried. Yield: 0.26 g (90%).

Physical measurements

Elemental analyses were carried out at the Laboratoire de Chimie de Coordination in Toulouse, France, for C, H, and N. IR spectra were recorded on a GX system 2000 Perkin-Elmer spectrophotometer. Samples were run as KBr pellets. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. All samples were 3 mm diameter pellets moulded from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 0.5 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.[19] Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibility has been computed by exact calculation of the energy levels associated with the spin Hamiltonian through diagonalization of the full

Table 1 Summary of crystal data and refinement details for **1**

Empirical formula	$C_{21}H_{20}CoCuN_4O_4S_2$
M	579.00
Temperature, K	200
Wavelength, Å	0.710 73
Crystal system, space group	Orthorhombic, *Pbca*
a, Å	11.587(2)
b, Å	18.303(4)
c, Å	21.919(4)
V, Å^3	4648.6(16)
Z	8
$\rho_{(calcd.)}$, Mg/m^3	1.655
μ_{Mo}, mm^{-1}	1.844
Crystal size, mm	0.15 × 0.13 × 0.08
θ range, deg	3.39 to 26.00
Number of reflections:	
Measured	32 631
Unique	4569 [$R_{int} = 0.1130$]
Number of refined parameters	300
Max. and min. transmission	0.867 and 0.770
GOOF for F^2	0.993
^aR ($I \geq 2\sigma(I)$)	0.0555
^bwR	0.0735
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^3	0.544 and −0.328

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w|F_o{}^2|^2]^{\frac{1}{2}}$.

Table 2 Selected bond lengths (Å) and angles (°)

Cu1–O2 1.952(3)	Cu1–O1 1.957(3)	Cu1–N1 1.970(4)	Cu1–N2 1.972(4)
Cu1–S2′ 2.766(2)	Co1–N3 1.957(5)	Co1–N4 1.980(5)	Co1–O2 2.020(3)
Co1–O1 2.023(3)	Co1–O3 2.438(4)	Co1–O4 2.484(4)	
O2–Cu1–S2′ 87.2(1)	O1–Cu1–S2′ 99.6(1)		
N1–Cu1–S2′ 97.2(1)	N2–Cu1–S2′ 92.0(1)		
O2–Cu1–O1 76.7(1)	O2–Cu1–N1 168.4(2)		
O1–Cu1–N1 91.9(2)	O2–Cu1–N2 92.2(2)		
O1–Cu1–N2 163.5(2)	N1–Cu1–N2 98.4(2)		
Cu1–O1–Co1 104.6(2)	Cu1–O2–Co1 104.9(2)		
N3–Co1–N4 126.3(2)	N3–Co1–O2 105.6(2)		
N4–Co1–O2 116.6(2)	N3–Co1–O1 109.5(2)		
N4–Co1–O1 113.0(2)	O3–Co1–O1 69.9(1)		
O2–Co1–O4 69.9(1)			

matrix with a general program for axial symmetry,[20] and with the MAGPACK program package[21] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.[22]

X-ray crystallography

Crystallographic measurements for $^{1}_{\infty}$[LCu^{II}Co^{II}(NCS)$_2$] (**1**) were carried out with the Oxford Diffraction XCALIBUR CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. The crystal was placed 60 mm from the CCD detector. Reflections of 612 frames were collected over 40 s with an ω angle between the frames of 0.75°. More than a hemisphere of reciprocal space was covered by combination of four sets of exposures; each set had a different φ-angle (0, 90, 180, 270°). Coverage of the unique set is 99.8% complete up to $2\theta = 52°$. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.[23] Intensity data were corrected for the Lorentz and polarization effects. The absorption correction was introduced by a semi-empirical method based on equivalent reflections, using the program MULTISCAN.[24] The structure was solved by direct methods using SHELXS-97[25] and refined by full-matrix least-squares on F_o with SHELXL-97[26] with anisotropic displacement parameters for non-hydrogen atoms. All H atoms were introduced in calculated positions with the isotropic displacement parameters fixed at $1.2 \times U_{eq}$ of the relevant carbon atom. Crystal data collection and refinement parameters are given in Table 1, and selected bond distances and angles are gathered in Table 2. CCDC reference number 293343. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518029e

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References

1 (*a*) *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1983, Vol. 3; (*b*) J. C. Bonner, in *Magneto-structural Correlations in Exchange Coupled Systems*, eds. R. D. Willet, D. Gatteschi and O. Kahn, NATO ASI Series 140, Reidel, Dordrecht, The Netherlands, 1985, p. 157; (*c*) *Magnetic Molecular Materials*, eds. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, NATO ASI Series 168, Plenum, New York, 1991.

2 (*a*) P. S. Mukherjee, S. Dalai, G. Mostafa, T. H. Lu, E. Rentschler and N. R. Chaudhuri, *New J. Chem.*, 2001, **25**, 1203; (*b*) P. S. Mukherjee, T. K. Maji, A. Escuer, R. Vicente, J. Ribas, G. Rosair, F. A. Mautner and N. R. Chaudhuri, *Eur. J. Inorg. Chem.*, 2002, 943.

3 C. P. Landee, in *Organic and Inorganic Low-Dimensional Crystalline Materials*, eds. P. Delhaes and M. Drillon, NATO ASI Series 168, Plenum, New York, 1987, p. 75.

4 Y. Pei, O. Kahn, J. Sletten, J. P. Renard, R. Georges, J. C. Gianduzzo, J. Curely and Q. Xu, *Inorg. Chem.*, 1988, **27**, 47.

5 J. P. Costes, F. Dahan, J. P. Laurent and M. Drillon, *Inorg. Chim. Acta*, 1999, **294**, 8.

6 J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama and T. Rojo, *Coord. Chem. Rev.*, 1999, **193–195**, 1027.

7 R. Cortes, M. Drillon, X. Solans, L. Lezama and T. Rojo, *Inorg. Chem.*, 1997, **36**, 677.

8 P. J. van Koningsbruggen, O. Kahn, K. Nakatani, Y. Pei, J. P. Renard, M. Drillon and P. Legoll, *Inorg. Chem.*, 1990, **29**, 3325.

9 R. Gheorghe, M. Andruh, J. P. Costes and B. Donnadieu, *Chem. Commun.*, 2003, 2778.

10 R. Gheorghe, P. Cucos, M. Andruh, J. P. Costes, B. Donnadieu and S. Shova, *Chem.–Eur. J.*, 2006, **12**, 187.

11 J. P. Costes, F. Dahan, A. Dupuis and J. P. Laurent, *Inorg. Chem.*, 1997, **16**, 3429.

12 The first sample was obtained accidentally by reaction of [LCuGd(NO$_3$)$_3$] with (Et$_4$N)$_2$[Co(NCS)$_4$] in 1/1 methanol/acetonitrile.

13 S. J. Gruber, C. M. Harris and E. Sinn, *J. Chem. Phys.*, 1968, **49**, 2183.

14 J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii and B. S. Tsukerblat, *J. Phys. Chem. A*, 1998, **102**, 200.

15 J. P. Costes, F. Dahan and J. Garcia-Tojal, *Chem.–Eur. J.*, 2002, **8**, 5430.

16 (*a*) R. Vicente, A. Escuer, E. Penalba, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 1997, **255**, 7; (*b*) R. Vicente, A. Escuer, J. Ribas and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1994, 259; (*c*) A. Escuer, S. B. Kumar, F. Mautner and R. Vicente, *Inorg. Chim. Acta*, 1998, **269**, 313.

17 A. M. Madalan, V. Ch. Kravtsov, D. Pajik, K. Zadro, Yu. A. Simonov, N. Stanica, L. Ouahab, J. Lipkowski and M. Andruh, *Inorg. Chim. Acta*, 2004, **357**, 4151.

18 V. Gutmann and K. H. Wegleitner, *Monatsh. Chem.*, 1968, **99**, 368.

19 P. Pascal, *Ann. Chim. Phys.*, 1910, **19**, 5.

20 J. M. Clemente-Juan, C. Mackiewicz, M. Verelst, F. Dahan, A. Bousseksou, Y. Sanakis and J.-P. Tuchagues, *Inorg. Chem.*, 2002, **41**, 1478.

21 (*a*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38**, 6081; (*b*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985.

22 F. James and M. Roos, "MINUIT Program, a System for Function Minimization and Analysis of the Parameters, Errors and Correlations", *Comput. Phys. Commun.*, 1975, **10**, 345.

23 CrysAlis RED, Oxford Diffraction Ltd., Version 1.170.32, 2003.

24 R. H. Blessing, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1995, **51**, 33.

25 G. M. Sheldrick, *SHELXS-97. Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1990.

26 G. M. Sheldrick, *SHELXL-97. Program for the refinement of crystal structures from diffraction data*, University of Göttingen, Göttingen, Germany, 1997.