SYNTHESIS AND CRYSTAL STRUCTURE OF THE FERROMAGNETIC CHAIN SYSTEM (C₆D₁₁ND₃)CuBr₃

G. C. DE VRIES, R. B. HELMHOLDT, E. FRIKKEE,

Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

K. KOPINGA, W. J. M. DE JONGE

Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

and

E. F. GODEFROI

Department of Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 17 November 1986; accepted 29 January 1987)

Abstract—The one-dimensional S = 1/2 Heisenberg ferromagnet $(C_6D_{11}ND_3)CuBr_3$, perdeutero cyclohexylammonium copper(II) bromide (CHAB-D₁₄), has been synthesized and its crystal structure has been determined with neutron diffraction. Like the chlorine isomorph CHAC, CHAB is orthorhombic, space group $P_{2_1}2_1$, z = 4, cell dimensions a = 19.561(8) Å, b = 8.678(4) Å, and c = 6.381(2) Å at 54.5 K. The ferromagnetic Cu-chains run along the *c*-direction. Two bromine ligands form symmetrical bridges between the copper ions. The bridging angles are 82.31 and 83.49° for the Cu-Br(2)–Cu and Cu-Br(3)–Cu bonds, respectively. Adjacent chains are well isolated from each other by the cyclohexyl groups in the *ac*-planes, and by the ND₃ moieties in the *bc*-planes.

Keywords: Crystal structure, synthesis, one-dimensional system, Heisenberg ferromagnet, neutron diffraction.

1. INTRODUCTION

During the last decades a number of good realizations of one-dimensional magnetic systems with various spin and exchange interactions (strength as well as sign) have been synthesized, leading to a considerable amount of experimental research in this area of 1D physics [1, 2]. Much theoretical work has been done in the relatively simple case of the onedimensional S = 1/2 spin system ("extreme quantum limit") with ferromagnetic nearest-neighbour interaction [3, 4]. A large effort has been devoted to the synthesis of these particular systems, ultimately resulting in a number of more or less 1D Cu²⁺ (S = 1/2) compounds [5]. The strong ferromagnetic coupling in these compounds results from the presence of symmetric Cu-X-Cu bridges with the Cu-X-Cu angle less than 90° (X = Cl, Br, O) [5–10]. At this moment one of the best realizations of the 1D S = 1/2Heisenberg-like ferromagnet is cyclohexylammonium copper(II) chloride ((C₆H₁₁NH₃)CuCl₃, CHAC), first synthesized in 1980 by Gaura et al. [5, 11]. The intrachain interaction in this compound amounts to $J/k_B = 45$ K with about 2% Ising anisotropy; the interchain interaction J' is three orders of magnitude smaller than J. A 3D magnetically ordered state is

induced below $T_N = 2.214$ K [12]. In 1982 Kopinga et al. [12] obtained single crystals of the bromine isomorph (C₆H₁₁NH₃)CuBr₃ (CHAB). Like CHAC, CHAB is an excellent 1D system with $J/k_B = 55 \pm 5$ K containing 5% XY anisotropy $(T_N = 1.50 \text{ K})$ [12, 13]. During the last years the magnetic properties of CHAC and CHAB have been extensively studied by means of magnetic specific heat [12, 14, 15], magnetization [11, 12, 16–18], susceptibility [16, 17], electron spin resonance (ESR) [13, 19, 20] and nuclear spin-lattice relaxation time (NSLR) measurements [14, 18]. These experiments demonstrated that at low temperatures the small anisotropies in J have a significant influence on both the magnetic excitation spectrum and the thermodynamic properties. ESR experiments on CHAC revealed that in addition to the normal linear spin waves there is evidence for the existence of so-called magnon bound states [13, 20]. In CHAB, the equation of motion of the spins can formally be transformed into a sine-Gordon equation because of the XY anisotropy in J. This equation allows non-linear soliton excitations [21-23]. Some evidence for the presence of this kind of excitation in CHAB has been obtained from magnetic specific heat, magnetization and NSLR experiments [14, 15, 18].

To enable studies on the static and dynamic magnetic properties of CHAB with neutron scattering techniques, we synthesized single crystals of the fully deuterated compound (C₆D₁₁ND₃)CuBr₃ (CHAB-D₁₄). Preliminary ferromagnetic resonance (FMR) and magnetization measurements on CHAB-D₁₄ yielded results identical to the corresponding ones for CHAB-H₁₄ within experimental accuracy. This suggests that deuteration hardly affects the magnetic properties. From neutron diffraction experiments a slightly larger value of the 3D antiferromagnetic ordering temperature $(T_N(CHAB-D_{14}) = 1.56 \text{ K})$ was found. The results of recent quasi-elastic neutron scattering experiments [24] could surprisingly be well described with the theoretical predictions of classical transfer-matrix calculations of the inverse correlation avoided by depositing a thin layer of GE 7031 varnish between the crystal and the sample holder and keeping the mounted crystals permanently at temperatures below -20° C.

The starting material in the synthesis of CHAB-D₁₄ is the commercially available deuterated compound aniline-D₇, C₆D₅ND₂. As a first step we produced cyclohexylamine-D₁₃, C₆D₁₁ND₂, following a procedure analogous to that documented in the literature for the production of hydrogenated cyclohexylamine, which will be briefly summarized below. The aromatic compound aniline can be hydrogenated with the aid of platinum-like catalysts to cyclohexylamine, C₆H₁₁NH₂. According to Greenfield [25] the reaction occurs stepwise under the formation of enamine and imine intermediates:



length, based on the spin Hamiltonian and interaction parameters inferred from heat-capacity and FMR experiments.

In section 2 of this paper we report on the synthesis of deuterated CHAB- D_{14} . The structure analysis by means of X-ray powder measurements on hydrogenated and deuterated compounds, and neutron diffraction experiments on a deuterated single crystal are described in section 3. The magnetic structure will be considered in section 4, whereas the paper is concluded with a discussion in section 5.

2. SYNTHESIS

In this section a brief survey of the synthesis of perdeutero cyclohexylammonium copper(II) bromide, (C₆D₁₁ND₃)CuBr₃, will be presented. CHAB-D₁₄ crystallizes by slow evaporation at room temperature from a solution with equimolar quantities of cyclohexylammonium bromide, C₆D₁₁ND₃Br, and copper(II) bromide, CuBr₂, in a solvent of partially deuterated n-propanol, C₃H₇OD. In this way a number of dark-purple CHAB-D₁₄ crystals were obtained, some of which had a mass of a few grams. However, in some production runs, as will be discussed in the last part of this section, we obtained pale needleshaped crystals instead. The long axis of the CHAB- D_{14} crystals coincides with the crystallographic caxis. At room temperature CHAB is stable in a dry-air atmosphere. However, the crystals seriously deteriorate when, at room temperature, the crystal surface makes direct contact with aluminium, which is commonly used as a material for the sample holder in neutron scattering experiments. This problem was The enamine and imine intermediates give rise to several additional reactions leading to the formation of, among others, dicyclohexylamine and at higher temperatures cyclohexane. These additional reactions also produce ammonia, NH_3 , which significantly inhibits the main-reaction by poisoning the catalyst. The addition of water, which is sometimes used to eliminate the toxicity of ammonia by converting it to the non-toxic ammonium cation [26, 27], is not feasible because this addition implicates the formation of cyclohexanone and, by reduction, cyclohexanol [28, 29].

We performed the deuteration of aniline- D_7 in a high-pressure (40 atm) batch reactor using a rhodium catalyst on γ -alumina, the temperature being stabilized at 60°C. After 12 h the reaction was interrupted, whereafter the cyclohexylamine- D_{13} was separated from the other reaction products by means of distillation. NMR-analysis of the final product showed a small fraction of hydrogen impurities, which are due to the fact that the starting material contained a few promille of aniline- H_7 . The second step was the production of deuterated cyclohexylammonium bromide. This was accomplished by evaporation of D_2O from an equimolar solution of cyclohexylamine- D_{13} and 47% DBr-solute in D_2O ,

$$\mathbf{D}_{3}\mathbf{O}^{+} + \mathbf{B}\mathbf{r}^{-} + \mathbf{C}_{6}\mathbf{D}_{11}\mathbf{N}\mathbf{D}_{2} \rightarrow \mathbf{C}_{6}\mathbf{D}_{11}\mathbf{N}\mathbf{D}_{3}\mathbf{B}\mathbf{r} + \mathbf{D}_{2}\mathbf{O}\uparrow.$$

To conclude this section a few remarks on the pale needle-shaped crystals will be given. X-ray powder measurements revealed significant deviations from the diffractogram of ordinary CHAB-D₁₄. Chemical analysis of the needles indicated a composition of $(C_6D_{11}ND_3)Cu_2Br_3$, which implies a reduction of Cu^{2+} to monovalent Cu^+ . This is corroborated by measurements of the susceptibility of some of these crystals, which revealed a diamagnetic behaviour. Attempts to prevent the growth of the needle-shaped crystals by creating an oxidizing environment (O₂ atmosphere) were unsuccessful.

3. STRUCTURE ANALYSIS

In order to determine the positions of the heavy atoms (i.e. all except H and D) in CHAB-H₁₄ and CHAB-D₁₄ we performed X-ray powder diffraction measurements on both compounds at 300 K. X-rays with a wavelength $\lambda = 1.5418$ Å were obtained from Ni-filtered CuK, radiation. The intensity was measured in 2θ -step scans, 2θ increasing from 3 to 73 deg with 0.02 deg/step. The data were analysed with a Rietveld profile refinement procedure, using the known values for CHAC [16] as starting parameters. With respect to the positions and isotropic temperature factors of the heavy atoms, only minor differences were found between the hydrogenated and deuterated compounds (and CHAC-H₁₄). The orthorhombic cell dimensions at 300 K for CHAB-D₁₄ [19.8400(23)] Å, [H₁₄] are: a = 19.8343(26)and c = 6.4405(6)b = 8.7804(9)[8.7778(8)] Å [6.4356(6)] Å. Zero layer Weissenberg photographs of a small single crystal of CHAB-D₁₄ unambiguously confirmed $P2_12_12_1$ as space group. This space group

† ACXR2	is	an a	absorption	correction	program	using
Gauss-quadr	atu	re to	calculate	the absorpti	on factor.	

is identical to that of CHAC, which corroborates the earlier assumptions based on the morphology of the single crystals and FMR rotation diagrams [13, 14, 24]. To complete the structure analysis, neutron-diffraction experiments were performed on a deuterated single crystal with approximate dimensions $1.7 \times 3.5 \times 3.8$ mm³. The crystal was mounted in a ⁴He-flow cryostat [30], the temperature being stabilized at $T = 54.5 \pm 0.5$ K. The data were collected on the four-circle diffractometer at the High-Flux Reactor at Petten. The neutron beam with a wavelength $\lambda = 1.2959$ Å was obtained from a Cu (220) double-monochromator system. From 13 highorder reflections the cell parameters were determined at 54.5 K: a = 19.561(8) Å, b = 8.678(4) Å and c = 6.381(2) Å. The intensity profile for each Bragg reflection was measured with $\omega/2\theta$ -step scans $(0.034 \text{ deg/step in } 2\theta)$. The typical measuring time per reflection was 20 min. Three reference reflections were measured repeatedly after every 50 reflections. The variations in the intensities of these reference reflections about their mean values were less than 2.7% and no systematic deviations could be observed. A total of 1377 independent reflections were measured (index range, h: 0-25, k: 0-11 and l: 0-7) for sin $\theta/\lambda < 0.64 \text{ Å}^{-1}$. The standard deviation in the structure factor, $\sigma(F_0)$, was obtained from counting statistics. Five reflections for which the structure factor was found to be smaller than $3\sigma(F_0)$ were excluded from the subsequent analysis. Absorption corrections were made using the program ACXR2,[†] for a crystal shape approximated by 14 lattice planes. The experimentally determined absorption

Table 1. (a)	Fractional p	ositional	coordinates	for	$(C_6D_{11}ND_3)CuBr_3$	at
54.5 K; (b)	Anisotropic	thermal	parameters	for	$(C_6D_{11}Nd_3)CuBr_3$	at
54.5 K						
Table 1a						

Atom	x	у	Ζ
Cu	0.2461(1)	0.0204(3)	0.1849(5)
B r(1)	0.2107(2)	0.2922(4)	-0.0056(5)
Br(2)	0.1561(2)	0.0218(4)	0.4538(5)
Br (3)	0.3189(2)	0.1389(4)	0.4543(5)
N	0.3238(1)	0.5826(3)	-0.0048(4)
C(1)	0.3970(2)	0.5378(4)	-0.0319(6)
C(2)	0.4257(2)	0.4769(5)	0.1729(6)
C(3)	0.4997(2)	0.4250(5)	0.1438(6)
C(4)	0.5057(2)	0.3045(5)	-0.0313(6)
C(5)	0.4754(2)	0.3650(4)	-0.2346(6)
C(6)	0.4015(2)	0.4186(4)	-0.2052(6)
D(N1)	0.2922(2)	0.4870(7)	0.0124(11)
D(N2)	0.3161(3)	0.6525(8)	0.1279(11)
D(N3)	0.3060(3)	0.6408(8)	-0.1386(11)
D (11)	0.4238(2)	0.6431(5)	-0.0781(8)
D(21)	0.3940(2)	0.3777(5)	0.2240(7)
D(22)	0.4221(2)	0.5655(6)	0.2961(8)
D(31)	0.5194(2)	0.3793(7)	0.2908(8)
D(32)	0.5314(2)	0.5251(6)	0.1053(8)
D(41)	0.4777(2)	0.1990(5)	0.0162(8)
D(42)	0.5598(2)	0.2721(6)	-0.0547(8)
D(51)	0.4765(3)	0.2753(6)	0.3573(8)
D(52)	0.5066(2)	0.4611(6)	-0.2923(8)
D(61)	0.3693(2)	0.3177(5)	-0.1616(8)
D(62)	0.3807(2)	0.4658(6)	-0.3514(7)

Table 1b

Atom	U_{11}	U ₂₂	U ₃₃
Cu	0.0121(11)	0.0104(12)	0.0082(13)
Br(1)	0.0124(13)	0.0098(14)	0.0099(15)
Br(2)	0.0107(13)	0.0113(13)	0.0111(16)
Br(3)	0.0129(14)	0.0101(14)	0.0108(16)
N	0.0135(11)	0.0094(11)	0.0112(13)
C(1)	0.0108(14)	0.0098(14)	0.0109(16)
C(2)	0.0106(14)	0.0187(16)	0.0138(17)
C(3)	0.0115(15)	0.0224(18)	0.0128(19)
C(4)	0.0178(17)	0.0183(18)	0.0175(18)
C(5)	0.0162(16)	0.0195(17)	0.0097(18)
C(6)	0.0144(15)	0.0130(15)	0.0147(19)
D(N1)	0.0403(26)	0.0451(29)	0.0524(34)
D(N2)	0.0438(29)	0.0550(35)	0.0461(34)
D(N3)	0.0438(29)	0.0497(33)	0.0519(37)
D (11)	0.0226(18)	0.0177(18)	0.0315(23)
D(21)	0.0235(19)	0.0295(21)	0.0214(21)
D(22)	0.0312(21)	0.0334(23)	0.0235(22)
D(31)	0.0279(21)	0.0470(28)	0.0253(25)
D(32)	0.0217(18)	0.0309(22)	0.0408(28)
D(41)	0.0350(21)	0.0198(19)	0.0338(25)
D(42)	0.0209(19)	0.0457(26)	0.0230(25)
D(51)	0.0368(23)	0.0362(25)	0.0256(23)
D(52)	0.0275(21)	0.0330(23)	0.0314(26)
D(61)	0.0220(17)	0.0179(18)	0.0326(23)
D(62)	0.0322(21)	0.0318(21)	0.0173(21)

Table 1b (cont)

U12	<i>U</i> ₁₃	U ₂₃	U _{eq}
-0.0006(11)	0.0016(10)	0.0004(11)	0.0102(7)
0.0031(12)	0.0005(12)	0.0006(14)	0.0107(8)
-0.0000(12)	0.0003(12)	0.0014(13)	0.0111(8)
-0.0014(12)	-0.0011(12)	-0.0004(13)	0.0113(8)
0.0007(10)	0.0000(10)	0.0005(12)	0.0114(7)
-0.0005(13)	0.0004(13)	-0.0014(14)	0.0105(8)
-0.0002(14)	-0.0012(13)	0.0021(16)	0.0144(9)
0.0021(15)	-0.0005(14)	-0.0014(17)	0.0156(10)
0.0058(15)	-0.0014(15)	0.0008(17)	0.0179(10)
0.0070(15)	0.0016(14)	-0.0023(16)	0.0151(10)
0.0047(15)	-0.0027(14)	-0.0011(15)	0.0140(9)
-0.0047(25)	0.0015(27)	0.0020(31)	0.0460(17)
0.0005(30)	0.0001(27)	-0.0112(34)	0.0483(19)
0.0051(28)	0.0018(28)	0.0044(34)	0.0485(19)
-0.0059(16)	0.0052(18)	0.0033(18)	0.0239(11)
-0.0016(18)	0.0032(16)	0.0104(18)	0.0248(12)
0.0044(19)	-0.0039(18)	-0.0141(20)	0.0293(13)
0.0112(21)	-0.0075(18)	0.0021(22)	0.0334(14)
-0.0077(19)	0.0004(19)	-0.0052(23)	0.0312(13)
0.0009(18)	-0.0019(20)	0.0046(22)	0.0295(13)
0.0153(19)	0.0015(18)	-0.0006(22)	0.0321(14)
0.0176(22)	-0.0013(20)	-0.0096(22)	0.0328(14)
-0.0007(20)	0.0118(19)	0.0102(22)	0.0307(13)
-0.0051(15)	-0.0004(18)	-0.0063(18)	0.0242(11)
0.0124(19)	-0.0024(19)	-0.0003(20)	0.0271(12)

The anisotropic temperature factor is defined as

$$\exp\left\{-2\pi^{2}[h^{2}(a^{*})^{2}U_{11}+k^{2}(b^{*})^{2}U_{22}+l^{2}(c^{*})^{2}U_{33}\right\}$$

 $-2\pi^{2}[h^{2}(a^{*})^{2}U_{11}+k^{2}(b^{*})^{2}U_{22}+l^{2}(c^{*})^{2}U_{33} + 2hka^{*}b^{*}U_{12}+2hla^{*}c^{*}U_{13}+2klb^{*}c^{*}U_{23}]\}.$

$$U_{eq} = \frac{1}{3} \sum_{i,j} U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

coefficient, μ , amounted to $0.74 \pm 0.05 \text{ cm}^{-1}$. The transmission coefficient, A^* , ranged from 0.810 to 0.886. For the least-squares refinement we used the program XFLS3, an updated version of ORFLS [31]. The scattering lengths were taken from a compilation by Koester and Yelon [32]. For the starting values of the heavy atom positions we used the coordinates found from our X-ray powder experiments, and for those of the deuterium atoms we used the hydrogen positions in CHAC reported by Groenendijk et al. [16]. The refinement of F_0 , involving the positional and anisotropic thermal parameters of all atoms, the scale factor and isotropic extinction (the total number of adjustable parameters, V, being 227), with weights $w = 1/{\sigma(F_0)^2 + 10^{-4} \times F_0^2}$ resulted in a final weighted $R_w = \sqrt{\Sigma w (F_0 - F_c)^2 / (\Sigma w F_0^2)}$ of 0.079 and a conventional $R = (\Sigma |F_0 - F_c|)/(\Sigma F_0)$ of 0.060. The residual $\chi = \sqrt{\Sigma w (F_0 - F_c)^2/(N - V)},$ for (N - V) = 1145 degrees of freedom, amounted to 5.30, the shift-to-error ratios in the last cycle of the refinement procedure all being smaller than 1%. The largest correction for extinction, yF_c , was y = 0.58[(200) reflection]. The final positional and thermal parameters of the atoms are given in Table 1. Important distances and angles are listed in Table 2.

The crystal structure of $CHAB(-D_{14})$ turns out to be completely analogous to the structure of CHAC. The system contains double-bridged linear chains along the *c*-axis built up from $CuBr_3^-$ ions (cf. Figs 1 and 2). The copper ions are located nearly exactly on the 2_1 -axis parallel to the *c*-axis and hence the apical Br(1) atoms lie alternately at opposite sides of the chain. The apical Cu-Br(1) bond length of 2.678 Å is significantly larger than the equatorial bonds Cu-Br(2) and Cu-Br(3) (2.459 and 2.427 Å, respectively) involved in the bridge formation. The above bond lengths are ca 0.12 Å larger than those in CHAC, as could be expected from the larger radius of the Br atom. The chains are hydrogen bonded in the *bc*-plane by the ND_3^+ moieties of the cyclohexylammonium groups (cf. Fig. 1). It has been shown previously that the structural properties of the metal-ligand bonds, such as the Cu-Br-Cu angle φ and the dihedral angle δ between the CuBr₂ moieties, are related to the magnitude and sign of the superexchange interaction between the metal atoms in the chain [5-10]. Semi-empirical molecular-orbital calculations indicate that symmetrical bridges with $\varphi < 90^{\circ}$ [6, 7] and dihedral angles deviating from 180° [10] favour strong ferromagnetic coupling. For CHAB-D₁₄ (CHAC-H₁₄) these values are $\varphi \approx 83^{\circ}$ (86°) and $\delta = 130.3^{\circ}$ (155.8°), respectively. The smaller angle δ for CHAB, in combination with the larger exchange interaction $J_{CHAB}/k_B = 55 \text{ K}$ vs $J_{\rm CHAC}/k_B = 45$ K, corresponds with the same trend observed in other copper(II) compounds [10]. Because of the strong hydrogen bonds with the apical Br(1) atom there is no significant overlap between the molecular orbital p_z of the bromide and the $d_{x^2-y^2}$ orbital of the unpaired Cu(II)-electron, thus pre-

venting efficient superexchange between adjacent chains in the *bc*-plane (the distance between the chains in this plane is 8.7 Å). In the *a*-direction the chains are separated by two layers of CHA-cations (the distance between the chains is 10.7 Å, cf. Fig. 2). There is no obvious superexchange path available, so the interchain interaction between chains in adjacent bc-sheets is expected to be mainly dipolar. Therefore it is not surprising that the values for the interchain interactions found from experimental data (magnetization measurements) and mean-field estimations [12, 16] are rather low (see Table 3 and Fig. 4). Figure 3 gives a perspective view of the total structure. In the figure the ab-plane and the c-axis are parallel and perpendicular to the drawing-plane, respectively. In the c-direction 9 unit cells have been drawn. For the sake of clarity the 11 deuterium atoms of each cyclohexylammonium cation have been omitted. Figcyclohexylammonium cation have been omitted. Figures 1, 2 and 3 were calculated and plotted using the program ORTEPII [33].

4. MAGNETIC STRUCTURE

Previous experiments have already established the relevant magnetic properties of CHAB. The small interchain interactions induce 3d long-range order, yielding a non-compensated antiferromagnetic spin array with a spontaneous moment along the adirection. In both CHAC and CHAB two symmetryrelated types of chains can be distinguished. FMR experiments [13] have shown that the spins are canted from the *b*-axis towards the *a*-axis by an angle $\varphi = \pm 25^{\circ}$ for CHAB and $\pm 17^{\circ}$ for CHAC (cf. Fig. 4). The fact that in CHAC this canting angle coincides with the angle between the Cu-Cl(1) bond and the b-axis, viz. 15.69°, as noted by Groenendijk et al. [16], must be accidental, since in the case of CHAB- D_{14} the angle between the Cu-Br(1) bond and the b-axis, viz. 16.89°, does not match the spin canting. The magnetic properties of the individual chains in both CHAC and CHAB can be described by the following Hamiltonian:

$$\mathscr{H} = -2\sum_{i} (J^{xx}S_{i}^{x}S_{i+1}^{x} + J^{yy}S_{i}^{y}S_{i+1}^{y} + J^{zz}S_{i}^{z}S_{i+1}^{z}),$$

with the values for the exchange parameters as listed in Table 3. The y-axis coincides with the crystallographic c-axis, whereas the x-axis is located within the *ab*-plane at an angle φ from the *b*-axis. The difference between the exchange-anisotropies in CHAB and CHAC is probably related to the small rearrangements in the equatorial Cu-X(2) and Cu-X(3) bonds. The almost perfect XY anisotropy in CHAB, evident from Table 3, must be accidental since there is no corresponding symmetry element in the space group. As already indicated in Ref. [24] the only magnetic space group belonging to the Opechowski family [34] of the space group $P2_12_12_1$, satisfying the requirements imposed by the experi-

Table 2. (a) Heavy atom bond distances and angles, the symbol ' indicates the second symmetry transformation; (b) deuterium bond distances and angles, the symbol ' indicates the second symmetry transformation Table 2a

Bond distances (Å	4)		
copper coordinati	on sphere	Bond angl	es (deg)
$C_{u}=Br(1)$	2 678(4)	Br(1)- Cu - $Br(2)$	98.81(14)
$Cu_Br(1)'$	3 519(4)	Br(1)-Cu-Br(2)'	94.72(14)
Cu = Br(2)	2 459(4)	Br(1)- Cu - $Br(3)$	97 96(14)
Cu = Br(2)'	2.455(4) 2.454(4)	Br(1) - Cu - Br(3)'	95.79(14)
Cu = Br(3)	2.434(4) 2.437(4)	Br(2) - Cu - Br(2)'	166 46(17)
Cu = DI(3)	2.727(7) 2.430(4)	Br(2) Cu $Br(2)$	86 30(14)
Cu-Di(5)	2.430(4)	$Br(2) = Cu = Br(3)^{\prime}$	91.86(15)
		Br(2)' - Cu - Br(3)	92 25(15)
		Br(2)' - Cu - Br(3)'	86 34(14)
		Br(3)-Cu-Br(3)'	166.24(17)
intrachain param	eters		
Cu–Cu′	3.234(4)	Cu'-Cu-Cu'	161.27(12)
		Cu–Br(2)–Cu′	82.31(13)
		Cu–Br(3)–Cu'	83.49(14)
cyclohexylammor	ium cation		
N-C(1)	1.494(4)	N-C(1)-C(2)	110.25(27)
C(1)-C(2)	1.518(5)	N-C(1)-C(6)	108.54(27)
C(2) - C(3)	1.528(5)	C(6)-C(1)-C(2)	111.65(29)
C(3) - C(4)	1 535(6)	C(1)-C(2)-C(3)	110.41(30)
C(4)-C(5)	1.520(6)	C(2)-C(3)-C(4)	111.21(31)
C(5) - C(6)	1.530(5)	C(3)-C(4)-C(5)	110.86(32)
C(0) = C(1)	1.517(5)	C(4) - C(5) - C(6)	111.65(31)
	11017(0)	C(5)-C(6)-C(1)	110.60(30)
		Table 2b	
Bond distances (A	Å)	Bond ang	les (deg)
$\mathbf{D}(\mathbf{N}(1) \mathbf{R}_{r}(1))$	2 327(7)	Br(1) D(N1) N	168 9(6)
$D(N_{2}) = B_{r}(1)'$	2.527(7)	Br(1)' = D(N2) = N	156 1(6)
D(N2)' Pr(1)	2.435(8)	Br(1) = D(N3)' = N'	160 1(5)
D(NJ) - DI(I)	1.041(6)	D(N1) - D(N2)	106.8(6)
D(N1) = N D(N2) = N	1.041(0)	D(N2) - N - D(N3)	109.2(6)
$D(N_2) = N$ $D(N_2) = N$	1.052(8)	D(N3) - N - D(N1)	105.8(6)
D(N3)-N	1.031(8)	D(143)-14-D(141)	105.8(0)
D(1)-C(1)	1.094(5)		
D(21) - C(2)	1.110(6)		
D(22)-C(2)	1.102(6)		
D(31)-C(3)	1.089(6)		
D(32) - C(3)	1.096(6)		
D(41)-C(4)	1.110(6)		
D(42)-C(4)	1.105(6)		
D(51) - C(5)	1.104(6)		
D(52)-C(5)	1.097(6)		
D(61)-C(6)	1.114(6)		
D(62)-C(6)	1.097(6)		
- () -(-)			

mental observations, is $P2_12_1'2_1'$. In Fig. 4 the magnetic symmetry elements of this space group are indicated.

5. CONCLUSIONS

The crystal structure of CHAB is isomorphic with the structure of CHAC. Furthermore, the crystallographic differences between the hydrogenated and deuterated versions of CHAB are very small. This is consistent with the conclusions from earlier FMR and magnetization experiments on CHAB-D₁₄ and CHAB-H₁₄, which indicated that the magnetic properties of these compounds are identical within experimental accuracy limits. The availability of deuterated CHAB offers the possibility to study an almost perfect realization of a ferromagnetic 1D S = 1/2 XXZ system by means of neutron scattering techniques. The first results of quasi-elastic neutron scattering experiments have recently been published [24]. At present, measurements are in progress to determine the magnon dispersion relation.

Acknowledgements—We would like to thank Mr. F. van Bolhuis, University of Groningen, for taking the Weissenberg photographs.



Fig. 1. Projection of the crystal structure of CHAB- D_{14} on the *bc*-plane. The chains along the *c*-axis are coupled by hydrogen bonding represented by the thin lines. The thermal ellipsoids correspond to 50% probability.



Fig. 2. Projection of the crystal structure of CHAB-D₁₄ on the *ac*-plane.



Fig. 3. Perspective projection of the crystal structure of $CHAB-D_{14}$. The *ab*-plane and the *c*-axis are parallel and perpendicular to the drawing-plane, respectively. In the *c*-direction 9 unit cells have been drawn.



Table 3. The exchange parameters of CHAB and CHAC [12, 13]. J is defined as $(J^{xx} + J^{yy} + J^{zz})/3$

	•		
		CHAB	CHAC
$\overline{J/k_B}$	(K)	55 <u>+</u> 5	45 ± 5
$(J^{xx} - J)/k_B$	(K)	0.92	0.52
$(J^{yy} - J)/k_B$	(K)	0.91	-0.01
$(J^{zz} - J)/k_B$	(K)	-1.82	-0.51
$z_{AF}J'_{AF}/k_B$	(K)	-0.03	-0.014
$z_F J_F / k_B$	(K)	0.15	0.08
φ	(deg)	25	17

REFERENCES

1. de Jongh L. J. and Miedema, A. R. Adv. Phys. 23, 1 (1974).

2. Steiner M., Villain J. and Windsor C. G., Adv. Phys. 25, 87 (1976).

- 3. Johnson J. D. and Bonner J. C., Phys. Rev. B 22, 251 (1980).
- 4. Schneider T. and Stoll E., Phys. Rev. B 25, 4721 (1982).
- 5. Willett R. D. and Landee C. P., J. appl. Phys. 52, 2004 (1981).
- Hay P. J., Thibeault J. C. and Hoffman R., J. Am. chem. Soc. 97, 4884 (1975).

Fig. 4. Schematic representation of the magnetic structure of CHAB (CHAC) in the *ab*-plane at T = 0 K. Each arrow represents the magnetic moment of a chain. There are two symmetry-related types of chain, I and II respectively. J'_{AF} denotes the antiferromagnetic interchain interaction between chains of type I and II, and J'_F denotes the ferromagnetic interchain interaction between chains of the same type.

- 7. Bencini A. and Gatteschi D., Inorg. Chim. Acta 31, 11 (1978).
- 8. Kahn O. and Briat B., J. chem. Soc. Faraday II 72, 268 (1976).
- 9. Crawford V. H., Wayne Richardson H., Wasson J. R., Hodgson D. J. and Hatfield W. E., *Inorg Chem.* 15, 2107 (1976).
- Charlot M. F., Kahn O., Jeannin S. and Jeannin Y., Inorg. Chem. 19, 1410 (1980).
- Willet R. D., Landee C. P., Gaura R. M., Swank D. D., Groenendijk H. A. and van Duyneveldt A. J., J. Magn. Magn. Mater. 15-18, 1055 (1980).
- 12. Kopinga K., Tinus A. M. C. and de Jonge W. J. M., Phys. Rev. B 25, 4685 (1982).
- Phaff A. C., Swüste C. H. W., de Jonge W. J. M., Hoogerbeets R. and van Duyneveld A. J., J. Phys. C 17, 2583 (1984).
- Kopinga K., Tinus A. M. C. and de Jonge W. J. M., Phys. Rev. B 29, 2868 (1984).
- Tinus A. M. C., de Jonge W. J. M. and Kopinga K., Phys. Rev. B 32, 3154 (1985).
- Groenendijk H. A., Blöte H. W. J., van Duyneveldt A. J., Gaura R. M., Landee C. P. and Willett R. D., *Physica* 106B, 47 (1981).
- 17. Hoogerbeets R., Abu Bakr E. H. and van Duyneveldt A. J., Physica 128B, 161 (1985).
- 18. Kopinga K., Tinus A. M. C. and de Jonge W. J. M., to be published.
- Hoogerbeets R. and van Duyneveldt A. J., *Physica* 121B, 233 (1983).
- 20. Hoogerbeets R., van Duyneveldt A. J., Phaff A. C.,

Swüste C. H. W. and de Jonge W. J. M., J. Phys. C 17, 2595 (1984).

- 21. Mikeska H. J., J. Phys. C 11, 129 (1978).
- 22. Mikeska H. J., J. appl. Phys. 52, 1950 (1981).
- 23. Etrich C. and Mikeska H. J., Z. Physik B 62, 97 (1985).
- Kopinga K., de Jonge W. J. M., Steiner M., de Vries G. C. and Frikkee E., Phys. Rev. B 34, 4826 (1986).
- 25. Greenfield H., J. org. Chem. 29, 3082 (1964).
- Maxted E. B. and Walker A. G., J. chem. Soc. (II), 1093 (1948).
- Maxted E. B. and Biggs M. S., J. chem. Soc. (III), 3844 (1957).
- Stork G. and White W. N., J. Am. chem. Soc. 78, 4604 (1956).
- Debus G. and Jungers J. C., Bull. Soc. Chim. Belges 62, 172 (1953).
- Herbert L. J. and Campbell S. J., J. appl. Cryst. 10, 18 (1977).
- ORFLS is a full-matrix least-squares program. It originates from Busing W. R., Martin K. O. and Levy H. A., Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
- Koester L. and Yelon W. B., Theory of Neutron Scattering from Condensed Matter (Edited by S. W. Lovesey), Vol. 1, p. 17. Clarendon Press, Oxford (1984).
- Johnson C. K., ORTEPII Report ORNL-3794, revised (1971), Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
- Opechowski W. and Guccione R., *Magnetism* (Edited by G. T. Rado and H. Suhl), Vol. 2A, Ch. 3. Academic Press, New York (1965).