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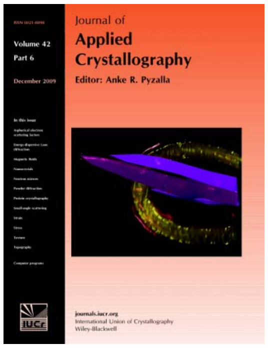

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The crystal structure of perdeuterated methanol monoammoniate ($CD_3OD{\cdot}ND_3$) determined from neutron powder diffraction data at 4.2 and 180 K

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The crystal structure of perdeuterated methanol monoammoniate, $CD_3OD{\cdot}ND_3$, has been solved from neutron powder diffraction data collected at 4.2 and 180 K. The crystal structure is orthorhombic, space group $Pbca$ ($Z = 8$), with unit-cell dimensions $a = 11.02320\ (7)$, $b = 7.66074\ (6)$, $c = 7.59129\ (6)$ Å, $V = 641.053\ (5)$ Å^3 [$\rho_{\rm calc} = 1162.782\ (9)$ kg m^{-3}] at 4.2 K, and $a = 11.21169\ (5)$, $b = 7.74663\ (4)$, $c = 7.68077\ (5)$ Å, $V = 667.097\ (4)$ Å^3 [$\rho_{\rm calc} = 1117.386\ (7)$ kg m^{-3}] at 180 K. The crystal structure was determined by *ab initio* methods from the powder data; atomic coordinates and anisotropic displacement parameters were subsequently refined by the Rietveld method to $Rp < 3\%$ at both temperatures. The crystal comprises a sheet-like structure in the *bc* crystallographic plane, consisting of strongly hydrogen bonded elements; these sheets are stacked along the *a* axis, and adjacent sheets are linked by what may be comparatively weak $C{-}D{\cdots}O$ hydrogen bonds. Within the strongly bonded sheet structure, ND_3 molecules are tetrahedrally coordinated by the hydroxy moieties of the methanol molecule, accepting one hydrogen bond ($O{-}D{\cdots}N$) of length $\sim$1.75 Å, and donating three hydrogen bonds ($N{-}D{\cdots}O$) of length 2.15–2.25 Å. Two of the methyl deuterons appear to participate in weak interlayer hydrogen bonds ($C{-}D{\cdots}O$) of length 2.7–2.8 Å. The hydrogen bonds are ordered at both 4.2 and 180 K. The relative volume change on warming from 4.2 to 180 K, $\Delta V/V$, is +4.06%, which is comparable to, but more nearly isotropic (as determined from the relative change in axial lengths, *e.g.* $\Delta a/a$) than, that observed in deuterated methanol monohydrate.

1. Introduction

The ammonia–methanol system presents an interesting counterpoint to the water–methanol system; the latter is of great importance in biological and industrial chemistry, and this system has been the subject of many experimental and computational studies. In contrast, very little study has been devoted to the ammonia–methanol system. A 1:1 complex of CH_3OH and NH_3 was identified in the gas phase by Millen & Zabicky (1962, 1965). This complex was subsequently studied experimentally using infrared spectroscopy (Hussein & Millen, 1974) and microwave spectroscopy (Fraser *et al.*, 1988). The 1:1 methanol–ammonia complex has also been studied computationally using classical potentials (Brink & Glasser, 1982) and quantum mechanical methods (Li *et al.*, 1997). Vapour–liquid equilibria in the ammonia–methanol system were measured by Inomata *et al.* (1988), Feng *et al.* (1999) and Schäfer *et al.* (2007), and the viscosity of the liquid was measured by Frank *et al.* (1996). The only known study of liquid–solid phase relations in the ammonia–methanol system is that of Kargel (1990, 1992), part of which is shown in Fig. 1. Kargel identified two solid compounds; these are methanol monoammoniate ($CH_3OH{\cdot}NH_3$), which melts congruently at 218.0 K, and methanol hemiammoniate ($2CH_3OH{\cdot}NH_3$), which melts incongruently at 194.6 K. Kanesaka & Kawai (1982) and Kanesaka *et al.* (1984) had earlier collected infrared spectra from frozen mixtures with a range of ammonia-to-methanol ratios at 77 K; this work did not identify whether the specimens were crystalline or amorphous, but the authors observed that the spectra did not change upon annealing.

Although this binary system has received almost no attention, the interaction between ammonia and methanol, in both the liquid and the solid state, provides a very simple archetypal system for understanding hydrogen bonding, particularly weak hydrogen bonds which may be donated by the methyl group, the latter having been the subject of long-standing debate (*e.g.* Steiner & Desiraju, 1998; Yukhnevich & Tarakanova, 1998). In our earlier structural analysis of methanol monohydrate, we discovered that the water molecules and hydroxy moieties of the methanol molecule participate in strong hydrogen bonds, forming a two-dimensional sheet-like structure. This sheet is decorated on its upper and lower surfaces by the hydrophobic methyl moiety of the methanol molecule; adjacent sheets are not hydrogen bonded, but interact only by weak van der Waals forces. This results in a very large volume thermal expansion coefficient, $527 \times 10^{-6}\ \mathrm{K}^{-1}$ at 160 K, the majority of which is due to interlayer expansion perpendicular to the strongly bonded sheets (Fortes *et al.*, 2007). Noting that methanol monoammoniate has a significantly higher melting point than any other solid in the ternary water–ammonia–methanol system (*cf.* Kargel, 1992), with the exception of water–ice, we had speculated that $CH_3OH{\cdot}NH_3$ has a relatively strong three-dimensional hydrogen-bond network rather than the two-dimensional network found in $CH_3OH{\cdot}H_2O$. There are few examples of cryocrystals that are structurally dominated by ammonia; the closest analogues to the methanol ammoniates may be the ammonia hydrates, which are fully three-dimensional hydrogen-bonded crystals (Loveday & Nelmes, 2000; Fortes, Suard *et al.*, 2009).

Lastly, both methanol and ammonia have been detected in the solid phase in interstellar and cometary ices, and may also be an important constituent of cryovolcanic liquids on the icy bodies in the outer solar system (Kargel, 1992; Lopes *et al.*, 2007). Hence, methanol ammoniates could be accessory mineral phases in a variety of extraterrestrial environments. Characterization of the crystal structures of these compounds is relevant to possible future *in situ* measurements of icy satellite mineralogy (*e.g.* Fortes, Wood, Dobson & Fewster, 2009).

We have collected neutron powder diffraction data from perdeuterated specimens of methanol monoammoniate and methanol hemiammoniate, with the objective of determining their crystal structures. The structure of neither ammoniate was known previously; in contrast to the monohydrate, there have been no prior X-ray studies to indicate the symmetry or unit-cell dimensions. This paper reports our results for methanol monoammoniate, and the structure of methanol hemiammoniate is reported elsewhere (Fortes, Wood & Knight, 2009).

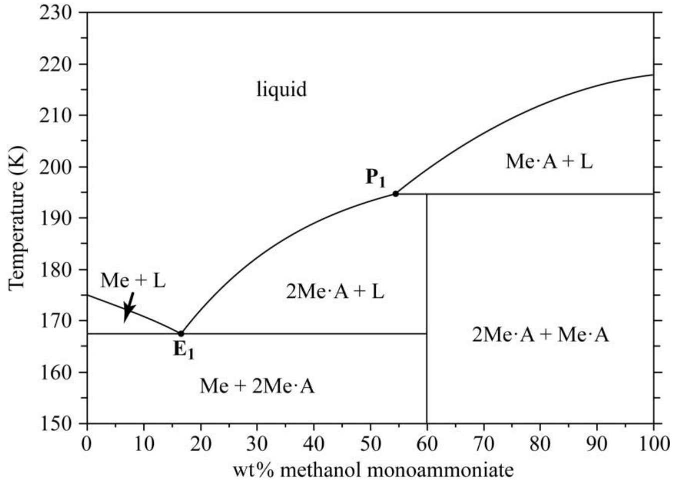

Figure 1
Liquidus and solidus phase boundaries at the methanol-rich end of the binary methanol–ammonia system, constructed using data reported by Kargel (1990). Me = methanol, 2Me·A = methanol hemiammoniate and Me·A = methanol monoammoniate. Eutectic $\mathbf{E_1}$ is at 167.2 K, 5.7 wt% NH_3, and peritectic $\mathbf{P_1}$ is at 194.6 K, 19.0 wt% NH_3. The ammonia-rich portion of the system is depicted by Kargel (1992).

The work described here was carried out on the High Resolution Powder Diffractometer, HRPD (Ibberson *et al.*, 1992), at the STFC ISIS neutron spallation source, Rutherford Appleton Laboratory, UK, which has the best combination of resolution and flux of any similar instrument in the world. Given the large incoherent scattering length of the H atom, a perdeuterated analogue, $CD_3OD{\cdot}ND_3$, was used in order to achieve good signal-to-noise in the measured diffraction data (*cf.* Finney, 1995).

2. Experimental

2.1. Sample preparation and data collection

An evacuated glass bulb immersed in a dry-ice-cooled acetone bath (~210 K) was used to condense 1.8764 g of liquid deuterated ammonia (Aldrich Chemical Co., 99 at% D). To this was added deuterated methanol (3.3811 g, Aldrich Chemical Co., 99.8 at% D) to form 5.2575 g of 1:1 molar stoichiometry solution (64.31 wt% CD_3OD). All of the solution in the bulb was poured into a stainless steel cryomortar pre-cooled to liquid nitrogen temperature, forming a toffee-like solid, which became brittle when liquid N_2 (L-N_2) was applied directly. This solid material was ground to a coarse powder very easily and then stored in a plastic container immersed in liquid nitrogen for ~24 h before the start of the diffraction experiment. All 5.25 g of the powdered solid was transferred to a pre-prepared[1] aluminium-framed slab can at L-N_2 temperature. The back window of the slab can was quickly screwed into place and the centre-stick/slab-can assembly was moved (with the sample immersed in an L-N_2 dewar) to an OC100 Orange cryostat on the HRPD beamline; a brief inspection (4.8 μAh) of the diffraction pattern at ~100 K revealed Bragg reflections, indicating that the specimen was crystalline, none of which could be attributed to either α- or β-methanol (Torrie *et al.*, 1989, 2002), or to cubic solid ammonia (Hewat & Riekel, 1979). The specimen was warmed to 180 K and data were collected in the 30–130 ms time-of-flight (t-o-f) window for 450.0 μAh, after which the choppers were re-phased to allow data collection in the 100–200 ms t-o-f window for 105.2 μAh. The short t-o-f window permits access to d-spacing ranges of 0.66–2.47 Å in HRPD's backscattering detectors ($2\theta = 168.33^\circ$), 0.92–3.45 Å in the 90° detector banks and 2.49–9.26 Å in the low-angle detectors

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[1] Before loading, the slab can was screwed to a cryostat centre stick and wired with heating elements and an RhFe resistance thermometer; the front window was screwed into place with a gadolinium/cadmium foil sandwich over the exposed aluminium frame and cadmium foil shielding around the exposed screw heads. The slab can was held in a shallow plastic dish of liquid nitrogen whilst the powder sample was loaded.

(average 2θ = 30°). In the long t-o-f window, the backscattering and 90° banks, respectively, view *d*-spacing ranges of 2.17–3.93 and 3.03–5.46 Å; no useful data were obtained in the low-angle bank with this flight time window. The temperature of the specimen was reduced to 4.2 K and data were collected in both the short (568.2 µAh) and the long (100.0 µAh) t-o-f windows. The specimen exhibited the same diffraction pattern at 4.2 K as observed at 180 K, albeit with slightly broader Bragg peaks and greatly reduced diffuse scattering at short *d* spacings (compare Figs. 2*a* and 2*c*).

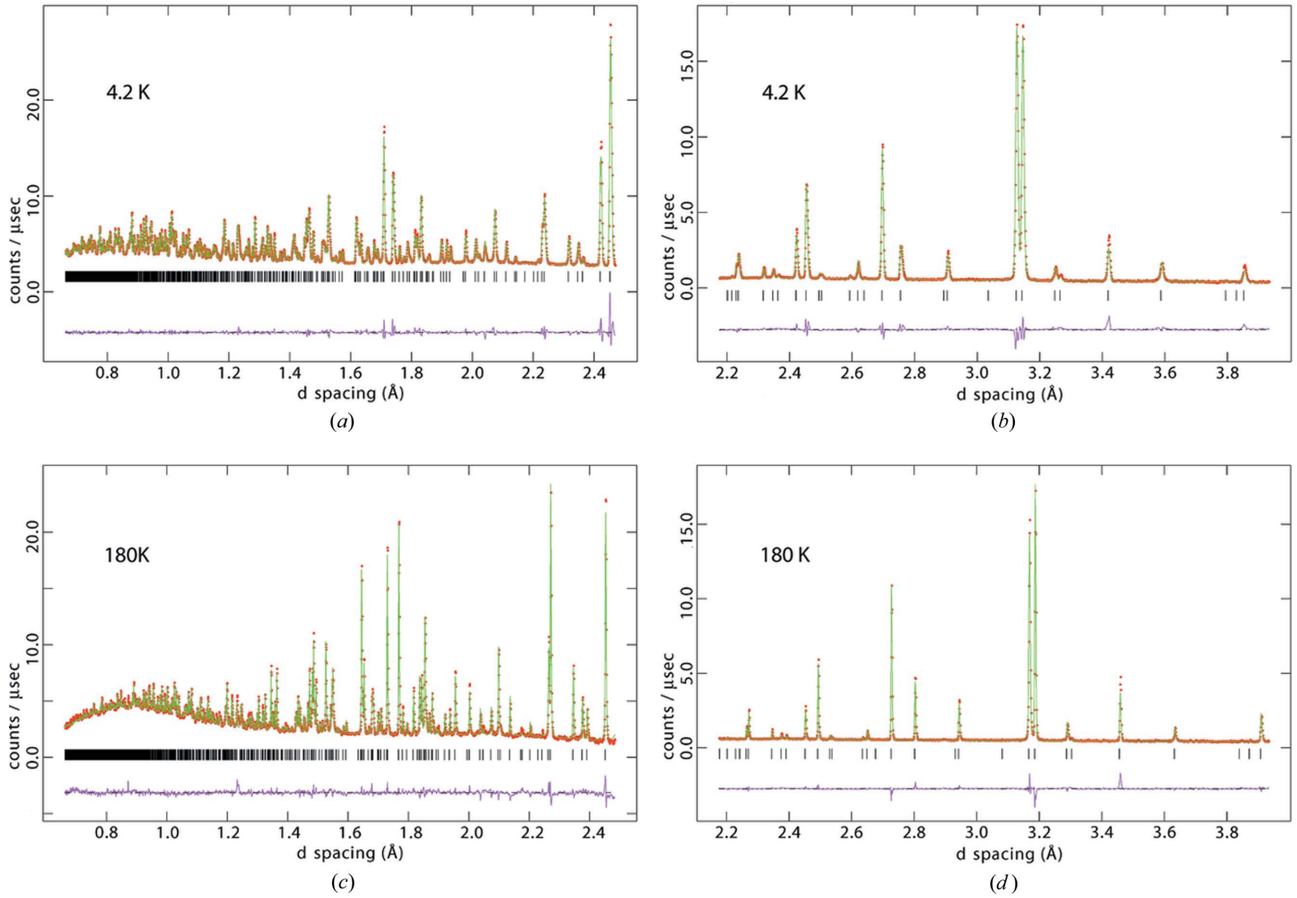
The diffraction data were normalized to the incident monitor spectrum, corrected for detector efficiency using a vanadium standard and exported as *GSAS*-format (Larsen & Von Dreele, 2000) raw files for analysis.

2.2. Indexing and structure solution

The 180 K backscattering data collected in the 100–200 ms t-o-f window was indexed using *DICVOL04* (Boultif & Louër, 2004), with an orthorhombic unit cell having dimensions a = 11.2134 (7), b = 7.7475 (5), c = 7.6812 (5) Å, V = 667.31 Å^3, the figures of merit being $M(20)$ = 83.7 (de Wolff, 1968) and $F(20)$ = 135.9 [0.0029, 50] (Smith & Snyder, 1979). Using the molecular volumes of CD_3OD in β-methanol at 170 K (53.63 Å^3; Torrie *et al.*, 2002) and of cubic ND_3 at 180 K (33.65 Å^3; Hewat & Riekel, 1979), we can obtain an estimate of the unit-cell volume as a function of the number of formula units per unit cell. The case of Z = 8 yields V = 698.24 Å^3, which differs from the indexed unit-cell volume by only 4.6%. That the solid compound is denser than a stoichiometric mixture of the two solid end-members is indicative of strong hydrogen bonding.

The most likely space-group – on the basis of systematic absences – was found to be *Pbca*; this requires that the asymmetric unit contains only one formula unit, which is in agreement with the inference made by Kanesaka *et al.* (1984).

The atomic structure was solved in space group *Pbca* from the 180 K powder data using the parallel tempering algorithm implemented in *FOX* (Version 1.6.99; Favre-Nicolin & Černý, 2002, 2004). Inputs for the solution process were the backscattering, 90° and low-angle diffraction patterns collected at 180 K in the 30–130 ms t-o-f window, along with profile coefficients determined by Le Bail fitting to the data with *GSAS*/*Expgui* (Larsen & Von Dreele, 2000; Toby, 2001), background points obtained by spline interpolation in *FOX* and definitions of the molecular fragments in the asymmetric unit in the form



(*a*) (*b*)

(*c*) (*d*)

Figure 2
Neutron powder diffraction patterns collected in the backscattering detectors of HRPD (2θ = 168.33°) from methanol monoammoniate at 4.2 K in the 30–130 ms t-o-f window (*a*) and the 100–200 ms window (*b*), and collected at 180 K in the 30–130 ms t-o-f window (*c*) and the 100–200 ms window (*d*). Note how much sharper the Bragg peaks are at 180 K, and the large diffuse background contribution at short *d* spacings; similar behaviour was observed in our study of methanol monohydrate upon cooling from 160 to 4.2 K.

Table 1
Refined structural parameters of methanol monoammoniate at 4.2 K.

		Fitted		Minus background	
Histogram	$N_{\rm data}$	*wRp*	*Rp*	*wRp*	*Rp*
Backscattering, 100–200 ms t-o-f	1974	7.15%	5.88%	9.02%	6.77%
Backscattering, 30–130 ms t-o-f	4385	2.25%	2.25%	3.00%	3.17%
Powder totals	6359	2.42%	2.86%	3.41%	4.00%
Reduced χ^2 = 19.85 for 128 variables					

Unit-cell dimensions	*a* 11.02320 (7) Å	*b* 7.66074 (6) Å	*c* 7.59129 (6) Å
Space group *Pbca*, *Z* = 8		*V* 641.053 (5) Å^3	$\rho_{\rm calc}$ 1162.782 (9) kg m^{-3}

Bond lengths and angles (Å, °) for the methanol molecule.

C—D1	1.080 (2)	D1—C—D2	109.74 (20)
C—D2	1.084 (2)	D1—C—D3	109.63 (22)
C—D3	1.061 (2)	D2—C—D3	105.65 (22)
C—O	1.425 (2)	O—C—D1	111.62 (14)
O—D4	1.011 (2)	O—C—D2	110.73 (18)
		O—C—D3	109.29 (17)
		C—O—D4	108.68 (17)
		D4—O—C—D3	178.72 (20)

Bond lengths and angles (Å, °) for the ammonia molecule.

N—D5	1.026 (2)	D5—N—D6	105.70 (19)
N—D6	1.006 (2)	D5—N—D7	108.22 (19)
N—D7	1.000 (2)	D6—N—D7	107.37 (17)

Hydrogen bonds and non-bonded intermolecular contacts (Å, °). The contact that is not considered to be a full hydrogen bond is shown in italics.

D4···N	1.746 (2)	O···N	2.757 (2)	O—D4···N	178.51 (17)
D5···O	2.152 (2)	N···O	3.176 (2)	N—D5···O	175.84 (16)
D6···O	2.211 (2)	N···O	3.205 (2)	N—D6···O	169.24 (16)
D7···O	2.256 (2)	N···O	3.235 (2)	N—D7···O	166.15 (17)
D1···O	2.709 (2)	C···O	3.754 (2)	C—D1···O	162.50 (16)
D2···O	2.782 (3)	C···O	3.861 (3)	C—D2···O	173.36 (17)
D3···O	*3.057 (2)*	*C···O*	*4.104 (2)*	*C—D3···O*	*169.23 (17)*
C···C	3.871 (3)				
O···O	4.578 (2)				
N···N	3.796 (2)				

Table 2
Refined structural parameters of methanol monoammoniate at 180 K.

		Fitted		Minus background	
Histogram	$N_{\rm data}$	*wRp*	*Rp*	*wRp*	*Rp*
Backscattering, 100–200 ms t-o-f	1974	4.69%	4.50%	7.15%	6.12%
Backscattering, 30–130 ms t-o-f	4403	1.67%	1.45%	2.43%	2.06%
Powder totals	6377	1.78%	1.67%	3.46%	2.87%
Reduced χ^2 = 9.623 for 107 variables					

Unit-cell dimensions	*a* 11.21169 (5) Å	*b* 7.74663 (4) Å	*c* 7.68077 (5) Å
Space group *Pbca*, *Z* = 8		*V* 667.097 (4) Å^3	$\rho_{\rm calc}$ 1117.386 (7) kg m^{-3}

Bond lengths and angles (Å, °) for the methanol molecule.

C—D1	1.022 (4)	D1—C—D2	105.8 (7)
C—D2	1.027 (5)	D1—C—D3	107.5 (6)
C—D3	0.991 (4)	D2—C—D3	107.8 (7)
C—O	1.390 (4)	O—C—D1	114.1 (4)
O—D4	0.970 (3)	O—C—D2	110.6 (4)
		O—C—D3	110.8 (3)
		C—O—D4	108.8 (3)
		D4—O—C—D3	179.7 (5)

Bond lengths and angles (Å, °) for the ammonia molecule.

N—D5	1.031 (3)	D5—N—D6	106.0 (3)
N—D6	0.975 (3)	D5—N—D7	107.0 (3)
N—D7	1.029 (3)	D6—N—D7	107.1 (3)

Hydrogen bonds and non-bonded intermolecular contacts (Å, °). The contact that is not considered to be a full hydrogen bond is shown in italics.

D4···N	1.784 (4)	O···N	2.753 (4)	O—D4···N	177.2 (3)
D5···O	2.169 (4)	N···O	3.197 (4)	N—D5···O	174.4 (3)
D6···O	2.311 (4)	N···O	3.273 (4)	N—D6···O	169.1 (2)
D7···O	2.257 (4)	N···O	3.262 (4)	N—D7···O	165.3 (3)
D1···O	2.855 (6)	C···O	3.796 (4)	C—D1···O	153.4 (4)
D2···O	3.025 (7)	C···O	4.047 (5)	C—D2···O	173.2 (5)
D3···O	*3.236 (6)*	*C···O*	*4.211 (4)*	*C—D3···O*	*168.1 (4)*
C···C	3.875 (4)				
O···O	4.636 (4)				
N···N	3.841 (3)				

of Z matrices. These Z matrices were created using the interatomic distances and angles found in solid α-methanol (Torrie *et al.*, 1989) and cubic ammonia (Hewat & Riekel, 1979); *FOX* was instructed to treat the molecules as rigid bodies. Twenty runs of 10 million trials each were performed, in which the crystal structure and the three diffraction patterns were optimized; these consistently produced very similar structures with chemically sensible molecular arrangements, and the structure with the lowest overall cost function was exported as a CIF to form the basis for Rietveld refinement with *GSAS*.

In *GSAS*, the initial structural refinements were carried out using only the 30–130 ms backscattering data, since these provide the highest *d*-spacing resolution and the highest atomic resolution (*i.e.* shortest *d*-spacing data) available. We had found previously (Fortes, 2006) that the early stages of structure refinement using the *FOX* output required the application of hard constraints on atomic coordinate and displacement parameter shifts, as well as stiff bond distance and angle restraints. In this instance, however, the refinement converged very smoothly without any bond restraints, proceeding quickly to the point at which all atoms could be refined with anisotropic displacement parameters. Final Rietveld refinement of this model at both 4.2 and 180 K was performed using the backscattering 30–130 and 100–200 ms t-o-f data combined. The data collected in the other detector banks were not used, since the 100–200 ms backscattering data extends to *d* spacings of 3.93 Å; only three weak reflections, measured in the 90° and low-angle detectors, exist at longer *d* spacings. The powder statistics and structural information obtained from these refinements are reported in Tables 1 and 2; the quality of the fit to the diffraction data is illustrated in Fig. 2.

3. Crystal structure of $CD_3OD{\cdot}ND_3$

The atomic coordinates and anisotropic displacement parameters are provided in the deposited CIF.[2] Inter- and intramolecular bond lengths and angles at 4.2 and 180 K are reported in Tables 1 and 2, respectively. The intramolecular bond lengths and angles of the ND_3 and CD_3OD molecules are in excellent agreement with those found in, respectively, solid ammonia and solid methanol (Table 3), indicating that these units are not significantly distorted by their inter-molecular bonds.

As shown in Fig. 3, the ND_3 molecule is tetrahedrally coordinated by the hydrophilic hydroxy moiety of the CD_3OD molecule. It accepts one O—D···N hydrogen bond of length 1.746 (2) Å at 4.2 K, and donates three N—D···O hydrogen bonds with lengths between 2.152 (2) and 2.256 (2) Å. The O—D···N contact is almost perfectly linear [178.5 (2)°], but the N—D···O contacts are slightly more bent, the angles ranging from to 166.2 (2) to 175.8 (2)°; nonetheless, these bonds are less bent than the N—D···N bonds in solid ammonia [160.0 (2)°]. The hydrogen-bond lengths and angles are typical for these donors and acceptors. The structure of ammonia monohydrate at 110 K (Loveday & Nelmes, 2000) is characterized by O—D···N hydrogen bonds of length 1.800 (3) Å and bond angle 176.0 (3)°; O—D···O hydrogen bonds of length 1.768 (6) Å and bond angle 176.0 (4)°; and N—D···O hydrogen bonds with lengths between 2.223 (4) and 2.366 (7) Å and bond angles between 156.6 (5) and 175.5 (2)°. Hence, in methanol monoammoniate the hydrogen bonds both donated to and accepted by the hydroxy moiety are generally stronger (*i.e.* shorter) than the equivalent hydrogen bonds donated to and accepted by the water molecule in ammonia monohydrate. That methanol is a stronger hydrogen-bond acceptor than water is to be expected since it is less acidic than the water molecule, although the difference in basicity is not as great as that between methanol and the highly acidic methanethiol. It would be of interest to examine the hydrogen bonding of thiol and selenol equivalents to the solid methanols, methanol monohydrate, methanol monoammoniate and methanol hemiammoniate, if these latter compounds exist.

The O—D···N bond length in solid methanol monoammoniate is significantly shorter – by approximately 13% – than the gas-phase O—H···N bond length of the ammonia–methanol complex computed from the microwave spectrum (Fraser *et al.*, 1988), which is 2.015 (2) Å. Similarly, the O···N contact in solid ammonia monohydrate is approximately 8% shorter than the spectroscopically determined gas-phase bond distance of the ammonia–water complex (Herbine & Dyke, 1985). In both cases, the increase in bond strength in the solid phase is attributed to hydrogen-bond cooperativity.

Table 3
Comparison of the molecular geometry (Å, °) obtained from the unrestrained structural refinement of methanol monoammoniate at 4.2 K (**B** and **D**) with the geometry of the CD_3OD molecule in α-methanol at 5 K (**A**; Torrie *et al.*, 2002), and the geometry of the ND_3 molecule in cubic ammonia at 2 K (**C**; Hewat & Riekel, 1979).

	Methanol molecule			Ammonia molecule	
	A	**B**		**C**	**D**
C—D1	1.091 (7)	1.080 (2)	N—D5	1.012 (2)	1.026 (2)
C—D2	1.084 (5)	1.084 (2)	N—D6	1.012 (2)	1.006 (2)
C—D3	1.068 (7)	1.061 (2)	N—D7	1.012 (2)	1.000 (2)
C—O	1.410 (4)	1.425 (2)			
O—D4	0.959 (6)	1.011 (2)			
D1—C—D2	108.4 (7)	109.7 (2)	D5—N—D6	107.5 (2)	105.7 (2)
D1—C—D3	108.3 (4)	109.6 (2)	D5—N—D7	107.5 (2)	108.2 (2)
D2—C—D3	108.7 (7)	105.7 (2)	D6—N—D7	107.5 (2)	107.4 (2)
C—O—D4	106.5 (5)	108.7 (2)			

The strongly hydrogen bonded ND_3 and OD units comprise a layer in the *bc* crystallographic plane (Fig. 4*a*); rather like the strongly bonded layers in methanol monohydrate, the hydrophilic components of the methanol molecule form an integral part of the layer, and the hydrophobic methyl groups are exposed on the upper and lower surfaces of the layer (Figs. 4*b* and 4*c*). The strongly hydrogen bonded layers are stacked along the *a* axis (Fig. 5). This places methanol molecules in adjacent sheets, related by the *b*-glide, in a 'top to tail' arrangement which results in the formation of what we infer to be weak C—D···O hydrogen bonds between two of the methyl deuterons (D1 and D2) and their nearest neighbour hydroxy O atoms. These bonds are comparatively long [D1···O = 2.709 (2) Å and D2···O = 2.782 (3) Å at 4.2 K] but they are remarkably linear [162.5 (2) and 173.4 (2)°, respectively], and are similar to the sum of the van der Waals radii of oxygen and hydrogen (2.72 Å; Bondi, 1964); arguably, directionality is a distinguishing characteristic of the hydrogen bond over the more isotropic van der Waals interaction. The

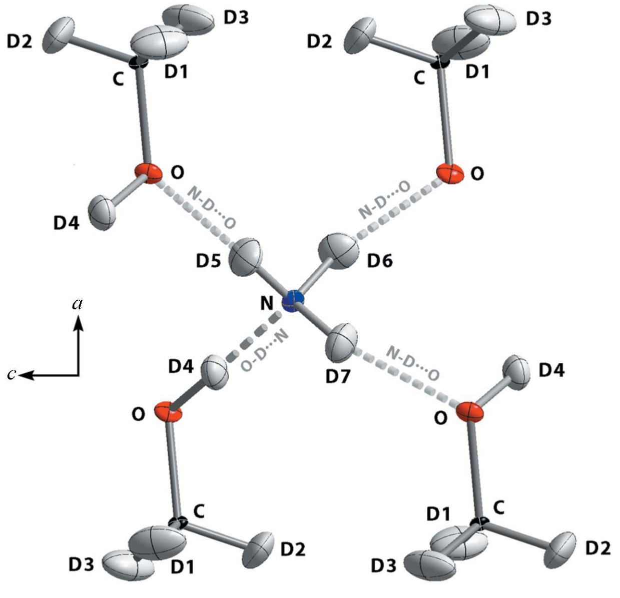


Figure 3
The atomic labelling scheme used in this work, illustrating (i) the refined displacement ellipsoids at 4.2 K (50% probability) and (ii) the tetrahedral coordination of the ND_3 molecules by CD_3OD molecules in the strongly hydrogen bonded sheet structure.

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[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DB5064). Services for accessing these data are described at the back of the journal.

question of whether such contacts can be considered as hydrogen bonds at all is the subject of long-standing debate (see Steiner & Desiraju, 1998, and references therein). Further experimental and computational analysis is required of the methanol monoammoniate structure in order to understand the possible significance of these proposed hydrogen bonds.

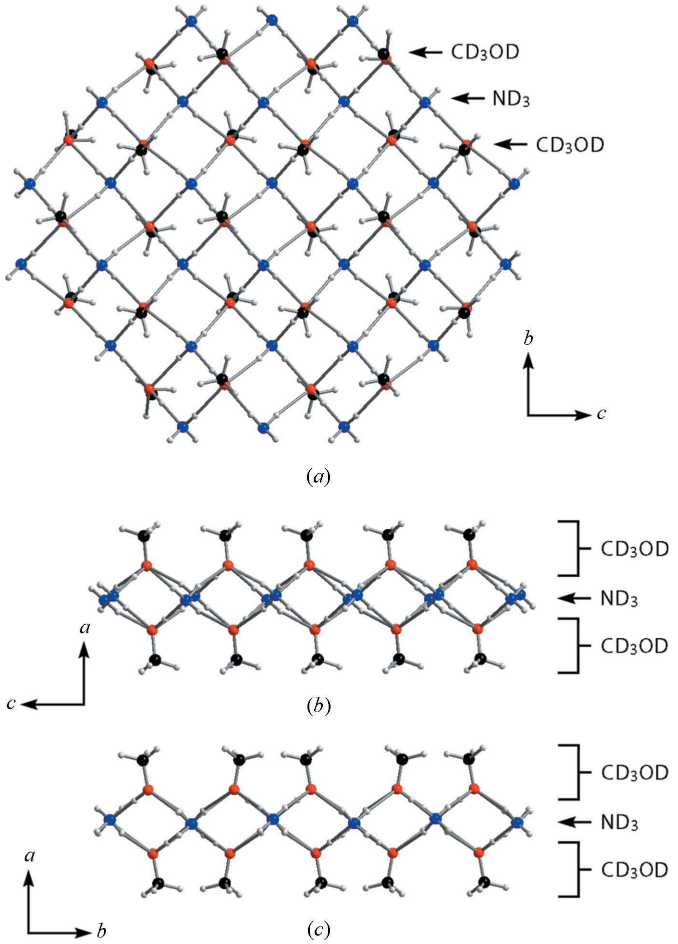

Figure 4
The strongly hydrogen bonded sheet structure in methanol monoammoniate, (*a*) viewed down the *a* axis, perpendicular to the plane of the hydrogen-bonded sheet; (*b*) viewed along the *b* axis, exactly parallel to the plane of the hydrogen-bonded sheet; and (*c*) viewed along the *c* axis.

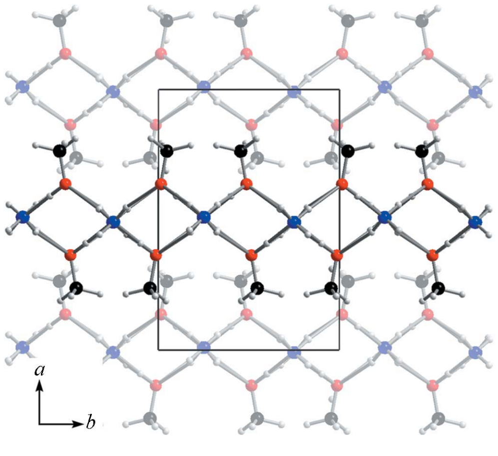

Figure 5
The unit cell of methanol monoammoniate viewed along the *c* axis, showing the strongly hydrogen bonded sheet structure (compare Fig. 4*c*) and its vertical stacking along the *a* axis.

The proposed weak C—D···O hydrogen bonds form a square net arranged at roughly 45° to the strong hydrogen bonds in the $ND_3\cdots OD$ layer (Fig. 6). Analogous C—D···O contacts are found in α-methanol at limiting low temperatures (Torrie *et al.*, 1989), with two of the methyl deuterons forming hydrogen bonds of length 2.512 and 2.647 Å, and bond angles 154.5 and 153.1°. We believe that the third methyl deuteron, D3, in methanol monoammoniate does not form a hydrogen bond. Its nearest neighbour is an N atom at a distance of 3.057 (2) Å at 4.2 K; whilst this contact is comparatively straight, C—D3···N = 169.2 (2)°, the length of the hydrogen bond is significantly greater than the sum of the van der Waals radii. In α-methanol, the third methyl deuteron has its nearest contact at a distance of 2.857 Å but the 'bond' angle is 132.5° (Torrie *et al.*, 1989). The hypothesis that this contact, which would crosslink the chains along the *c* axis, is not a hydrogen bond is supported by the very large thermal expansion of α-methanol along the *c* axis compared with the other two axes (see §4 and Table 4).

4. Thermal expansion of $CD_3OD{\cdot}ND_3$

Since data were collected at widely spaced temperatures, it is possible to obtain some information concerning the volumetric and axial thermal expansion of methanol monoammoniate. The relative volume change, $\Delta V/V$, upon warming from 4.2 to 180 K is +4.06%, which – as shown in Table 4 – is comparable to the volume expansion found over a similar temperature range in other ammonia–methanol and water–

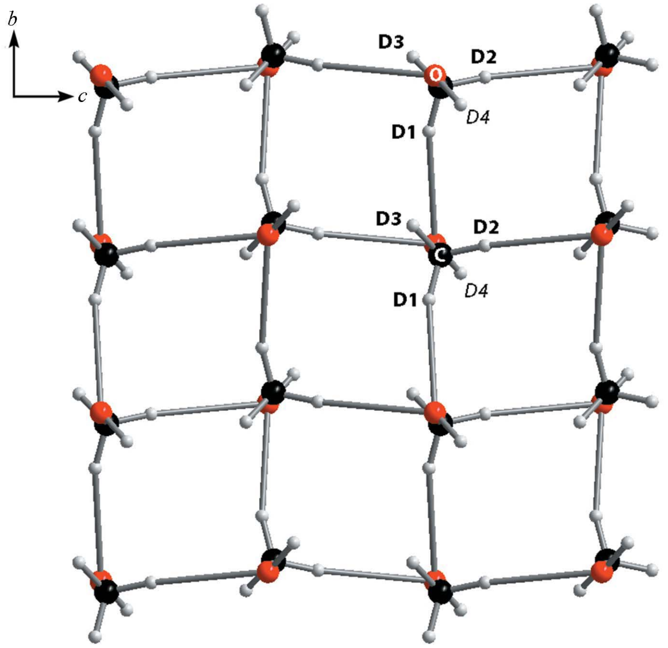

Figure 6
View down the *a* axis showing the net of weak purported hydrogen bonds formed between methanol molecules of adjacent layers in the structure.

Table 4

Relative axial and volumetric changes (%) from low to high temperature in the orthorhombic crystals of perdeuterated methanol monoammoniate, methanol hemiammoniate, methanol monohydrate, α-methanol and cubic ammonia; also shown are the relative volume changes observed in perdeuterated water ice, ammonia dihydrate and ammonia hemihydrate.

Note that $\Delta V/V$ is considerably larger in the more weakly hydrogen bonded substances (upper row), and that the directions perpendicular to the non-hydgrogen-bonded layers in methanol monohydrate and α-methanol experience the greatest axial expansivities (highlighted in bold).

	$CD_3OD{\cdot}ND_3$ 4.2–180 K[a]	$2CD_3OD{\cdot}ND_3$ 4.2–180 K[b]	$CD_3OD{\cdot}D_2O$ 4.2–160 K[c]	α-CD_3OD 15–160 K[d]	ND_3 2–180 K[e]
a axis	+1.71	+1.56	−0.30	+1.26	+1.55
b axis	+1.12	+1.40	**+3.47**	+0.29	n/a
c axis	+1.18	+1.12	+1.20	**+2.79**	n/a
Volume	+4.06	+4.14	+4.39	+4.59	+4.65

	D_2O (ice Ih) 4.2–160 K[f]	$ND_3{\cdot}D_2O$ 4.2–160 K[g]	$2ND_3{\cdot}D_2O$ 4.2–160 K[h]
Volume	+0.45%	+2.03%	+3.58%

References: (*a*) this work; (*b*) Fortes, Wood & Knight (2009); (*c*) our unpublished work (see Fortes, 2006; ISIS experimental report RB610064); (*d*) Torrie *et al.* (1989, 2002); (*e*) Hewat & Riekel (1979); (*f*) Fortes *et al.* (2008); (*g*) Fortes *et al.* (2003); (*h*) our unpublished work.

methanol compounds, as well as solid methanol and solid ammonia, but it is much larger than in non-methanol-bearing compounds. The expansion along each of the crystallographic axes is similar, indicative of comparatively isotropic thermoelastic properties, and supporting the observation of a fully three-dimensional hydrogen-bonded crystal. This contrasts with both methanol monohydrate and α-methanol, in which one crystallographic direction is dominated by weak van der Waals interactions instead of hydrogen bonds, resulting in a large thermal expansion along that direction, and thus a large anisotropy.

The O—D···N and N—D···O hydrogen bonds exhibit a comparatively small degree of expansion on warming from 4.2 to 180 K. However the purported C—D···O hydrogen bonds expand by 5–9% over this temperature range. In order to better characterize the thermal expansion of this substance from base temperature to its melting point, and to understand the role of molecular vibrations in driving that expansion, it will be necessary to make high-precision measurements of the unit-cell dimensions using neutron powder diffraction, and to collect single-crystal neutron diffraction data, both as a function of temperature.

5. Summary

The structure of perdeuterated methanol monoammoniate has been determined from neutron powder diffraction data collected at 4.2 and 180 K. The crystal comprises strongly hydrogen bonded layers formed by ND_3 and the OD group of the methanol molecule, which are orientationally ordered. These appear to be linked together by weaker hydrogen bonds between the CD_3 and OD groups of methanol molecules in adjacent layers. We see no evidence of the orientational disorder of the methyl groups observed in methanol hemiammoniate (Fortes, Wood & Knight, 2009). The thermal expansion over the range 4.2–180 K is more nearly isotropic than that observed in methanol monohydrate. This newly determined crystal structure contains a range of hydrogen-bond donors and acceptors of fundamental interest to physical chemists, and provides a natural laboratory for investigating these interactions.

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