ARTICLE TYPE

Negative 2D thermal expansion in the halogen bonded acetone bromine complex.

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The crystal structure of the complex formed between acetone and bromine has been determined between 14K and 200K. The structure exhibits negative 2D thermal expansion at low temperature and colossal thermal expansion in the
10 **perpendicular dimension. At low temperature the C=O bond is significantly longer than that observed in free acetone.**

Most materials expand upon heating and for molecular solids values of the linear expansion coefficient comparable to that seen in ice 55 MK^{-1} (at 250 K)[1], are typical. When the value of the
15 linear expansion coefficient is greater than 100 MK^{-1} such expansion is called colossal thermal expansion[2]. Much rarer is the phenomena of negative thermal expansion (NTE) that occurs when a material contracts upon heating[3,4]. It is possible for materials to exhibit both positive and negative thermal expansion
20 in different directions[5]. Although rarer, NTE has been observed in a variety of materials such as zeolites[6], metal oxides[7], metal fluorides[8], and cyanides[9,10], however in molecular solids NTE is much rarer[11-13]. Recently we have shown that the halogen bonded complexes PyICl and PyIBr[13](py= pyridine) undergo colossal
25 thermal expansion (147 and 176 MK^{-1}) coupled with negative thermal expansion in another direction.

We have previously determined the structure using neutron powder diffraction (110K) of one the best-known halogen bonded complexes namely that between acetone and bromine[14] which
30 consists of chains of acetone and bromine molecules. Linking these molecules are strong halogen bonds between the acetone and bromine. Our results showed that the presence of a short intermolecular O----Br bond was accompanied by the elongation of the Br-Br bond, a result which had not been observed in an
35 earlier study[15]. In addition to these changes, we observed small changes in bond length within the C=O groups, but not at a statistically significant level, whilst on a macroscopic level colossal thermal expansion was observed. Our objective in this study was to carry out an accurate low temperature study to
40 obtain a more accurate value for the C=O bond length and a thermodiffractometric study to investigate the thermal expansion of this material together with the structural changes that accompany heating.

The complex was prepared by mixing stoichiometric quantities
45 of perdeuteroacetone and bromine at 0 ℃. The mixture was pipetted into a pre-cooled (0 ℃) vanadium can fitted with a thin

walled quartz liner into which some amorphous quartz-glass wool had been placed. The vanadium can was sealed and cooled on a block of solid CO_2 prior to loading into a cryostat on the high
50 resolution powder diffractometer at the ISIS facility. The sample was cooled to base temperature and 45 short data collections to obtain lattice parameters were made between 14 K and 200 K, in order to obtain information on the magnitudes and directions of the thermal expansion tensor. These short runs were interspersed
55 with 4 longer runs. These longer runs were carried out with the intention to obtain accurate structural parameters in addition to the lattice parameters.

The use of neutrons as our radiation source has enabled us to obtain more accurate positions of the atoms with low atomic
60 number in this complex and hence dimensions for the acetone molecule. This is because of the comparable magnitudes of the coherent scattering lengths of C, D, O and Br. This would not be the case, in an X-ray structure determination, where the structure factors would be dominated by the scattering from the bromine
65 atoms.

Lattice parameters were obtained by using Model independent fits[16], and the structural parameters were obtained by Rietveld refinement[17]. Selected interatomic contacts are given in Table 1, diagrams of the molecular structure are shown in Figure 1,
70 difference Rietveld plots are available as supplementary material.

The structure at all temperatures is similar to that which we have previously described[14], and there is good agreement for the Br-Br and O---Br distances with a recent theoretical study on this system[18]. In particular, there are two short O---Br interactions,
75 for each acetone molecule, such that the bromine molecules are positioned towards the lone pairs of the oxygen atoms with a Br----O----Br angle of approximately 110°. All of these contacts are significantly shorter than the sum of the van der Waals radii of bromine and oxygen (3.45 Å[19]). These interactions result in
80 syntactic chains being formed. These chains lie parallel to the (1 0 -1) plane giving rise to a sheet structure (Figure 2). It is to be noted that there are no strong intermolecular interactions between the chains that build up the layers of the sheet. In addition to these intermolecular interactions, there are also C-D---Br and C-
85 D---O weak hydrogen bonds, the latter of which occur between the layers. At all temperatures the Br-Br bong lengths are longer than observed in in either Br_2 vapour (2.28105 Å[20]) or pure bromine in the solid state (2.286(3) Å[21]) with the difference being particularly pronounced at low temperature.

It should be noted that an earlier study on solid bromine showed that the bond length of the Br_2 molecules in the solid phase varies significantly as a function of temperature so that whilst at 5 K it is 2.301(2) Å (which is comparable to our 200K measurement), at
5 250K it is 2.286(3), this was accompanied by an increase in the intermolecular Br---Br contacts which expand from 3.286 Å (5 K). to 3.368 Å (250 K).
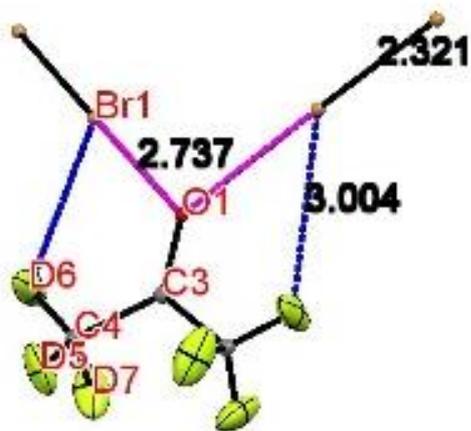
10 Figure1 Structure illustrating Br---O and C-D---Br interactions Distances in Å
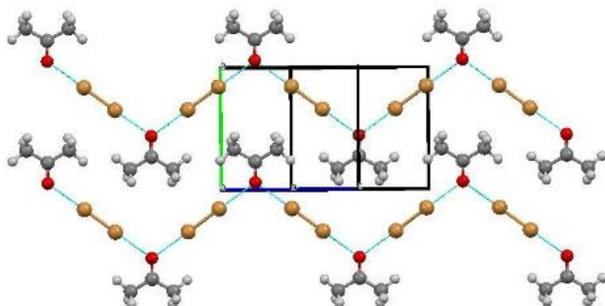
Figure 2 Plane of molecules (1 0 -1 plane)
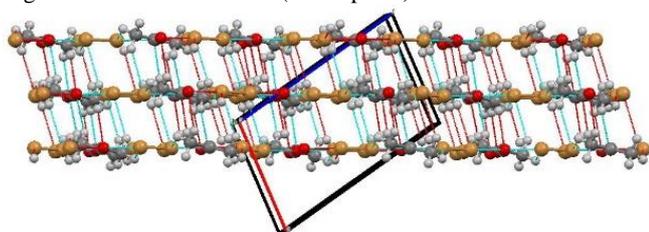
Figure 3 View showing weak hydrogen bonds between layers

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Table 1 Selected interatomic contacts/Å

Temp/K	C=O/Å	Br-Br/Å	O---Br/Å	Br---O---Br/°
14	1.248(4)	2.321(3)	2.737(2)	109.3(1)
35	1.243(3)	2.327(3)	2.734(2)	109.5(1)
75	1.250(4)	2.328(3)	2.737(2)	110.1(1)
110†	1.230(3)	2.322(2)	2.748(2)	110.5(1)
200	1.227(6)	2.309(5)	2.797(4)	110.1(2)

†[14]

A similar trend is observed in this study with short O---Br
20 intermolecular contacts being accompanied by the greatest elongation of the Br – Br bond and occurring at low temperatures. For our lowest temperature measurements the C=O bond is significantly longer than seen in either our previous 110 K neutron structure 1.230(3)Å[14], or the 200K structure (this work).
25 The C=O bond length (110K) was at the longer end of the range of values reported for structures of acetone. For the purposes of comparison, the most pertinent of these were those given in a NPD structure refinement of pure deuteroacetone in which C=O bond lengths of 1.213(4) Å and 1.202(4) Å were determined for
30 the two independent molecules in the asymmetric unit[22].

We now turn to the thermal expansion properties of the material Figures 4-7 show the variation of lattice parameters, and unit cell volume with temperature. From these graphs it can be clearly seen that both the a and b axis undergo negative thermal
35 expansion at very low temp temperatures but positive thermal expansion at higher temperatures. Fitting a quadratic function of temperature over the range 14 – 75 K for both a and b give the point at which positive thermal expansion starts at 42K and 35K respectively. Whilst these plots are informative in establishing
40 the occurrence of phenomena such as negative thermal expansion it has been pointed out that it is more useful to use the principal axes of the expansion tensor to extract information on the expansion properties[23]. Consequently, We have analysed the lattice parameter data using the computer program PASCAL[24].
45 Because of the occurrence of negative thermal expansion at low temperature we have analysed the data for two separate temperature ranges; the low temperature range 14 to 37 K, and the higher temperature range 47 to 200K. The thermal expansion coefficients and the normalised components of the principal axes
50 projected onto the crystallographic axes, are given in Table 3, together with diagrams showing the thermal expansion for each of these temperatures regimes (Figure 8). Plots of material pertaining to the thermal expansion are available as supplementary information.

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Table 2 Selected contacts involving deuterium

Temp/K	D6---Br1/Å	D7---Br1/Å	D5---O/Å
14	3.004(3)	3.017(3)	2.672(3)
35	2.994(3)	3.024(3)	2.666(2)
75	2.976(4)	3.049(3)	2.661(3)
110†	3.001(3)	3.060(4)	2.680(3)
200	2.986(7)	3.119(5)	2.777(5)

†[15]

Table 3

Temperature Regime 14 – 37 K

Axes	α MK⁻¹	σα MK⁻¹	a	b	c
X_1	-39.6	6.3	-0.9997	0	0.0244
X_2	-18.2	6.0	0.0	1.0	0.0
X_3	157.6	2.2	0.3617	0.0	0.935
V	109.6	12.9			

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Temp Regime 47   200 K

Axes	α MK⁻¹	σα MK⁻¹	direction		
			a	b	c
X_1	42.4	0.5	0.9733	0	0.2295
X_2	67.3	2.1	0.0	-1.0	0.0
X_3	169.3	3.3	-0.2682	0.0	0.9634
V	284.6	5.5			

One of the striking features of this material is the occurrence at low temperature of negative thermal expansion in two dimensions together with positive thermal expansion in the third. The larger of these contractions lies close to [-1 0 0] and the smaller is along [0 1 0]. It has been pointed out that the occurrence of negative thermal expansion in two dimensions whilst accompanied by thermal expansion in the third giving rise to negative 2D expansion is itself quite rare[23,24,25] and has only been seen in a limited number of materials[26-30] for example MOF's[23] LiBeBO$_3$[25], Group 10 cyanides[26], graphite[27], the low temperature form of
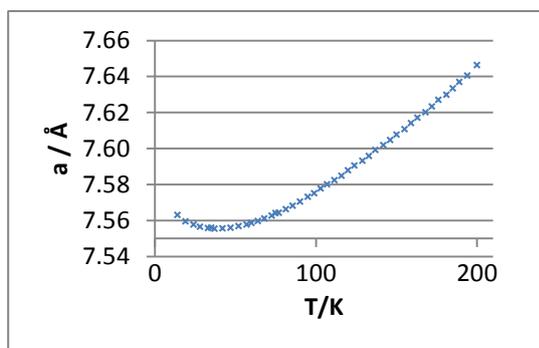
Figure 4 Variation of a /Å with T/K for (CD$_3$)$_2$CO-Br$_2$ Complex
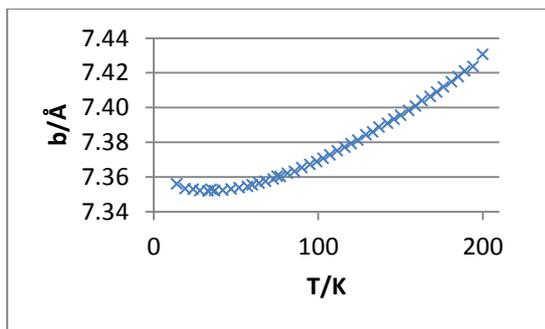
Figure 5 Variation of b /Å with T/K for (CD$_3$)$_2$CO-Br$_2$ Complex
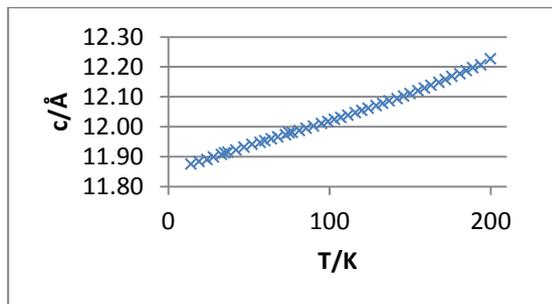
Figure 6 Variation of c /Å with T/K for (CD$_3$)$_2$CO-Br$_2$ Complex

arsenic[28], low temperature β 2,4-dinitroanisole[29], 1-ethyl-2,3-dimethylimidazolium bromide[30] and the lithium aluminosilicate, petalite[31]. In addition to the negative 2D expansion there is colossal expansion in the third direction. In the low temperature regime it can be seen that the colossal expansion occurs close to the [1 0 3] direction. In order to more clearly formulate the factors responsible for this behaviour we have attempted to associate these macroscopic expansion properties with specific

intermolecular interactions.

At first sight (figure 2) it would appear that the bonds associated with expansion in the [1 0 3] direction are the intermolecular O---Br bond, and intramolecular Br-Br bonds, together with the changes in the angle between 2 O---Br halogen bonds. However The 1-3 O---O distance has the same value 7.793 Å at 14 and 35 K.

We believe that the expansion correlates primarily at low temperatures with the reduction in the C4-D7---Br interactions, but the C4-D5---O hydrogen bond which also acts across the layers strengthen slightly. The net result is that adjacent chains
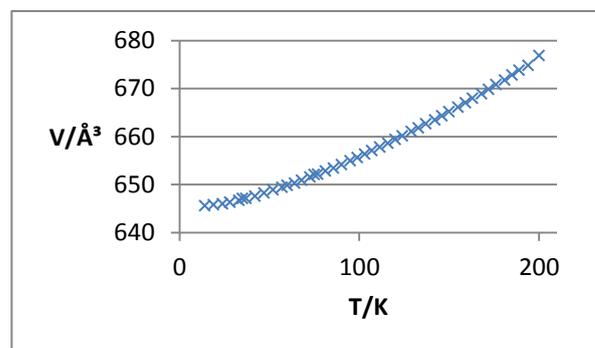
Figure 7 Variation of V /Å^3 with T/K for (CD$_3$)$_2$CO-Br$_2$ Complex
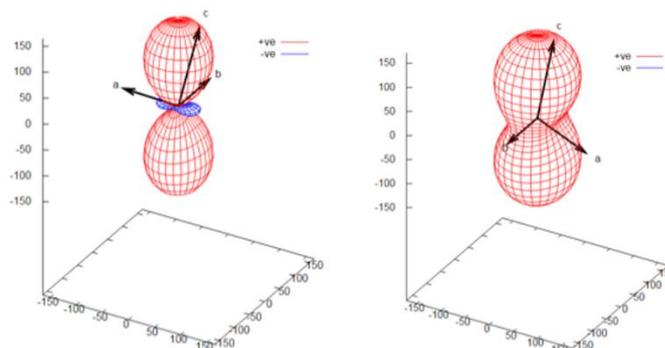
Figure 8 Expansivity Indicatrix for low(left) and high (right) temperature regions

move with respect to each other. This accompanied by the slight increase in the Br---O---Br angle which can be seen to expand as the temperature is raised (Table 1) At higher temperatures the C-D---O interaction also significantly weakens (Table 2) and is furthermore accompanied by weakening of the O---Br halogen bond (Table 1). These features are accompanied by increasing thermal motion of the methyl group further weakening these out of plane interactions and can be seen by the increase in thermal notion of methyl groups (supplementary data). At low temperatures there appears to be strengthening of the C-D---O interactions and it can be seen that there is a large component of this bond is parallel to a, this would suggest that negative expansion would result at the lowest temperature.

Finally it can be seen that the interaction C-D6---Br persists even at 200K. This interaction is situated within the layers, which explains its persistence, as increasing motion of the methyl

groups will not significantly affect its ability to interact with the bromine atoms. This may also account for the negative expansion at low temperatures as this bond is approximately parallel to b. However, at higher temperatures increasing thermal motion of the methyl groups leads to increasing separation between the double chains within the layer. Thus the switching off in turn of each of these interaction explains in part the expansion properties.

Finally, some comment should be made about the observed carbonyl bonds lengths. At all temperatures the C=O double bond length is somewhat longer that in acetone in the gas state $1.212(2)^{32}$. The bonding of acetone as an η^1 ligand to metal ions is well known. We have compared the bond lengths in our low temperature structures to a series of metal atoms in which there are no d-orbitals available for back bonding as this could complicate any inferences we could draw about the metal ---O bond because of potential back bonding into the π^* orbitals of the carbonyl group. We examined the C=O distances when acetone was coordinated to a s-block, p-block or lanthanide metal ions and in all cases the C=O bonds found in the database were shorter[33]. It has been pointed out that elongation of the C=O double bond can result from either a dipolar CO----M interaction or from formal donation to form a dative bond[34].

Thus whilst lengthening of the C=O bond cannot prove formal donation, longer C=O bond lengths are accompanied by longer Br-Br distances at low temperature. When the temperature is raised both bond lengths are shortened and are accompanied by an increase in the O----Br distance. The simplest explanation for this behaviour is that there is significant electronic donation from the oxygen to the Br_2 molecule forming the halogen bond, as this would account for both the elongation of the C=O and Br_2 bonds and shortening of the O---Br distance as these bonds become stronger at the lower temperatures. At higher temperatures these weak bonds are disrupted by increasing thermal motion, as we have noted earlier, leading to interactions that are more dipolar in nature. This accounts for both the changes in bond length but also being in accord with the model we suggest to explain the macroscopic expansion behaviour.

In conclusion we have shown that the use of variable temperature neutron powder diffraction has enabled us to observe that the interplay of relatively weak intermolecular C-D---O, C-D---Br hydrogen bonds and C=O---Br halogen bonds are responsible for the occurrence of the rare phenomenon negative 2D expansion at low temperatures in this compound. Furthermore the use of neutron diffraction has enabled us to show that the C=O bond as determined in the three low temperature structures we studied is significantly lengthened with respect to free acetone, strongly suggesting the interaction between oxygen and bromine involves more than a simple electrostatic interaction.

Notes and references

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