research papers

An order–disorder phase transition in the structure of C_{60}·4benzene

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A reversible, broad, order–disorder phase transition in the structure of C_{60}·4benzene has been observed to take place with an inflection point at 134 K. In the low-temperature structure fullerene disorder is removed, although the average atomic displacement parameters differ for the two C_{60} molecules in the asymmetric unit. Some benzene disorder persists, even at 13 K.

1. Introduction

The distinctive, grainy, needle-like crystals of the [60]fullerene benzene solvate C_{60}·4benzene are frequently encountered when benzene solutions of C_{60} are evaporated. They are soft and readily lose benzene in air with the loss of crystallinity. Indeed, in the first report of the isolation of C_{60}, Krätschmer *et al.* (1990) published a photograph of crystals like those considered here that were obtained by evaporation of a benzene solution. The first single-crystal study of this compound to be reported (Meidine *et al.*, 1992), carried out at 173 K, showed large anisotropic displacement parameters localized in the carbon cage. A second study (Balch *et al.*, 1993) based on data collected at 104 K described the structure as having two rotationally disordered C_{60}'s of relative occupancy 55:45, three ordered benzenes and one disordered benzene in a triclinic unit cell with $Z = 2$. A subsequent study (Bürgi *et al.*, 1994) made use of this data and examined the unusually large domain occupied by benzene in the structure. It is well known that primitive, cubic crystals of [60]fullerene are disordered at room temperature and undergo a phase transition to a partially ordered phase at 249 K. Further cooling results in a transition to a glassy state, and thus full ordering never occurs (Heiney *et al.*, 1991; Johnson *et al.*, 1992; Bürgi *et al.*, 1992; Babu & Seehra, 1992). Due to the pattern of hexagons and pentagons in [60]fullerene, there is no optimal arrangement that is compatible with closest packing, and disorder is the inevitable result of this frustration. Numerous investigations have shown that solid [60]fullerene exhibits correlated rotational motion, and theoretical models have attempted to relate this motion to van der Waals interactions between neighbors. Are there preferential arrangements between the pentagons and hexagons in neighboring balls? Since the structure of unsolvated [60]fullerene lacks order and is subject to twinning, the lower-temperature, ordered structure of C_{60}·4benzene offers some insights into this question.

2. Experimental

Owing to their instability in air, crystals of C_{60}·4benzene were removed from vials still containing a minimum of the mother liquor, covered with Paratone oil, and quickly mounted on the

Table 1
Experimental details.

For all structures: $C_{60} \cdot 4C_6H_6$, $M_r = 1033.03$, triclinic, $P\bar{1}$. Experiments were carried out with Mo $K\alpha$ radiation using a Bruker SMART 1000 diffractometer. H-atom parameters were constrained.

	(I)	(II)	(III)
Crystal data			
Temperature (K)	157	93	13
a, b, c (Å)	9.9555 (10), 15.0855 (15), 17.5006 (19)	9.9217 (13), 15.044 (2), 34.807 (4)	9.8842 (12), 15.0159 (19), 34.691 (4)
α, β, γ (°)	65.258 (6), 88.309 (5), 74.854 (4)	65.371 (7), 88.254 (5), 74.912 (4)	65.377 (3), 88.098 (3), 74.812 (2)
V (Å^3)	2294.5 (4)	4541.8 (10)	4500.2 (10)
Z	2	4	4
μ (mm^{-1})	0.09	0.09	0.09
Crystal size (mm)	$0.32 \times 0.28 \times 0.24$	$0.32 \times 0.28 \times 0.24$	$0.35 \times 0.09 \times 0.08$
Data collection			
Absorption correction	None	None	None
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25 185, 10 483, 6327	60 046, 26 819, 16 366	20 798, 20 479, 6542
R_{int}	0.040	0.044	0.055
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.139, 0.483, 1.81	0.053, 0.145, 0.98	0.050, 0.091, 0.71
No. of reflections	10 483	26 819	20 479
No. of parameters	472	1561	1501
No. of restraints	1	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.92, −0.49	0.43, −0.32	0.25, −0.22

Computer programs used: *SMART* (Bruker, 2002*a*), *SAINT* (Bruker, 2002*b*), *SHELXS*97, *SHELXL*97, *SHELXTL*5.1, *XP* (Sheldrick, 2008).

goniometer. Using a Bruker SMART CCD instrument, a CRYO Industries low-temperature apparatus and an Mo sealed tube source, three different crystals were examined. The crystals were taken through the phase transition three times to verify reversibility of the intensities and unit-cell dimensions. Data was collected at 93 K and also at 157 K. A different crystal was used for measurements at 13 K, which employed a CRYO Industries He cryostat. Variable-temperature measurements were carried out using a Siemens P3 diffractometer equipped with a serial (1-D) detector, LT-2
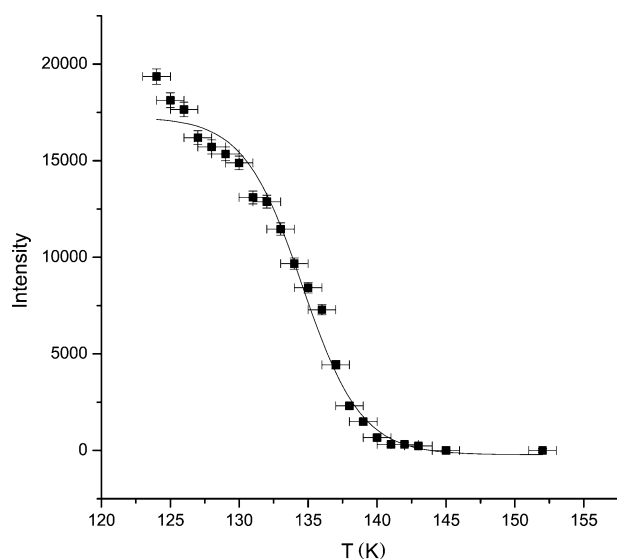
Figure 1
The intensity of the (543) reflection (indexed in the unit cell with the c axis doubled) as the temperature is raised.

low-temperature apparatus, and Siemens Cu rotating anode. A set of 12 reflections was measured at each of 22 temperatures ranging from 124 to 154 K. A wait of 5 min at each new temperature was sufficient to obtain reproducibility. The intensities of seven strong reflections with odd values of l in the cell with $c' = 2c$ (the low-temperature cell) and five reflections with even values of l were followed. A data set was also collected at 142 K on this instrument. At this temperature, the disorder consists of two primary orientations but there remains significant residual density that cannot be modelled, and the $R1$ value was 0.15. Solution of the structure at 157 K from scratch was unsuccessful, but a starting solution was obtained from the disordered model previously published (Balch *et al.*, 1993). At the initial stage of structure solution, two C_{60}'s, treated as rigid groups, were employed and the $R1$ value was 0.238. The addition of three more groups, based on fitting of difference map peaks to further rigid C_{60} groups reduced the $R1$ value to 0.195, 0.157 and 0.139, sequentially. In the refinement the C_{60}'s were retained as rigid groups but their isotropic displacement parameters were allowed to vary. The occupancies were restrained to sum to 1.000. With five different orientations included in the model the $R1$ value was still high and the first 20 difference map peaks, all in the C_{60} shell, added up to 14.8 e Å^{-3}, an indication that some residual density remained to be assigned. The largest peak had a value of 0.92 e Å^{-3}. However, correlation effects at this stage had begun to be significant, and it was felt that little could be gained by continuation of this process. In the final refinement, five rigid balls were included with refined occupancies of 0.149 (3), 0.243 (4), 0.139 (4), 0.318 (5) and 0.150 (4) for sets a–e, respectively. The main purpose of this exercise was to
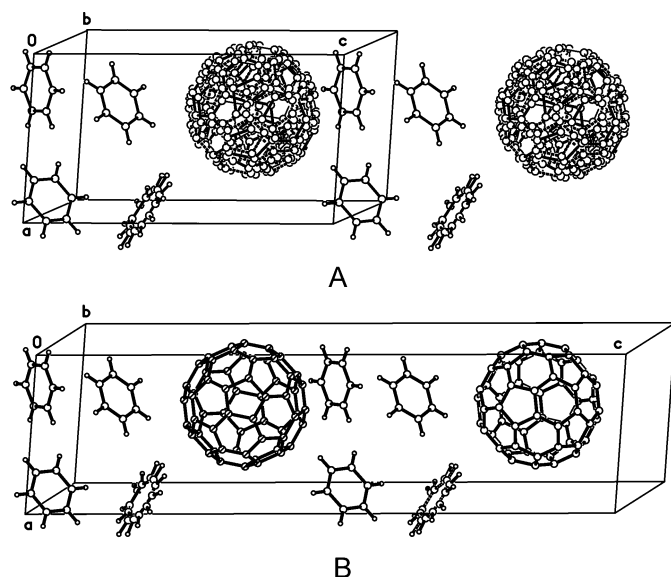
Figure 2
Plot A depicts a view of the 157 K unit cell with five orientations of C_{60}. Plot B shows the fully ordered fullerene structure at 93 K with a doubling of the c axis.

illustrate the large degree of disorder and we do not purport to have determined a fully optimized arrangement.

In striking contrast to the structure at high temperature, the solution and refinement of the structure at 93 and 13 K, employing a triclinic unit cell with $c' = 2c$, was trivial and showed two fully ordered C_{60} molecules and eight molecules of benzene in the asymmetric unit. Two of the benzene molecules are disordered by a rotation of 30° in the plane of the benzene molecule. One of the four benzenes is similarly disordered at high temperature. All non-H atoms were refined with anisotropic displacement ellipsoids except those of the disordered benzene. A test of the models in the non-centrosymmetric space group $P1$ did not lead to a stable refinement, thus all refinements were carried out in $P\bar{1}$. A summary of crystal data is given in Table 1.

3. Results

A representative plot of the intensity of a reflection indexed in the low-temperature cell with odd values of l as a function of T is shown for (543) in Fig. 1. Similar plots were obtained for six additional reflections with odd values of l. The average inflection point for all seven plots was 134 K. The phase transition takes place over a range of approximately ±10° above and below this point. We found a linear increase in intensity of five reflections with even l of 1.6% K^{-1} as the temperature was lowered. The curve shown is not corrected for this linear change. Representative plots are given in the supplementary material.[1]

A view of the unit cell before and after the phase transition is shown in Fig. 2. The centers of the two balls are nearly superimposable by a $\frac{1}{2}$ translation of the second ball along c with a 0.086 Å displacement between them. The 0.086 Å centroid displacement, after allowing for a $\frac{1}{2} c$ translation in the 93 K structure, agrees with the 0.085 Å displacement reported by Bürgi in the 104 K refinement.

In $C_{60}\cdot 4$benzene the percentage shrinkage in the three crystallographic axes between 157 and 13 K is $a = 0.71$, $b = 0.44$, $c = 0.87$%. Benzene-to-benzene contacts are changed
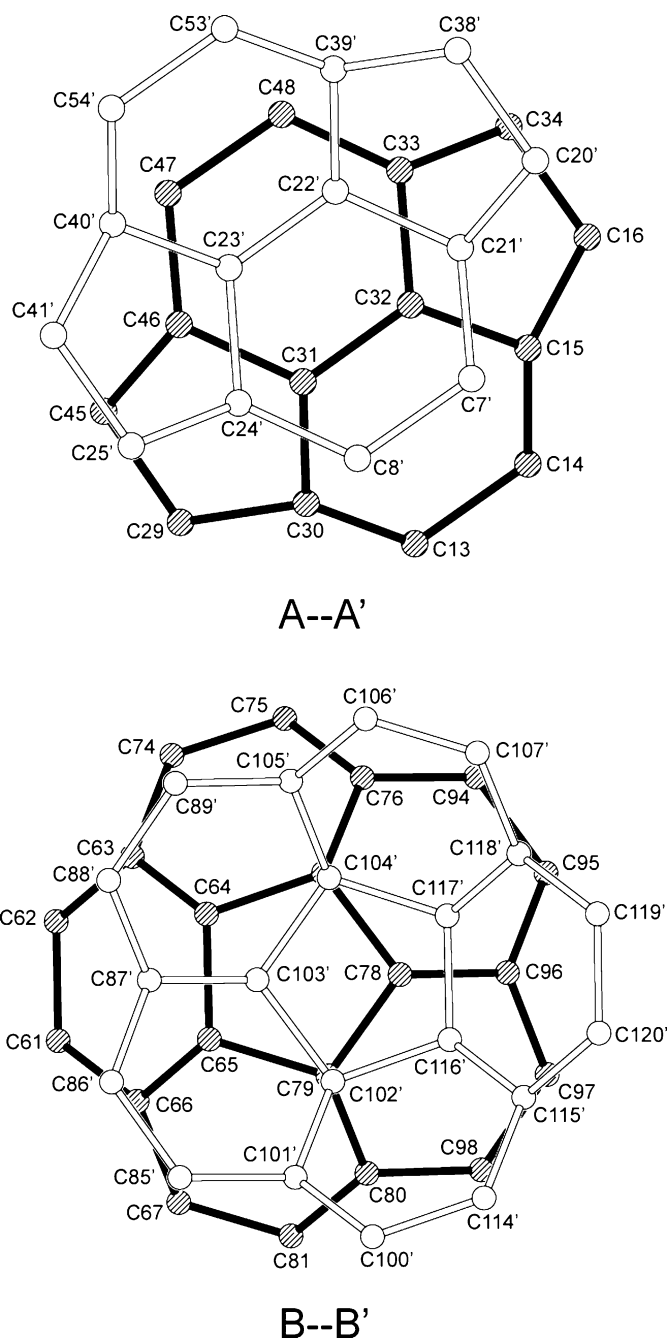

A--A'

B--B'

Figure 3
Ball-to-ball contacts between C_{60} molecules in the rotationally ordered structures.

little. In the **a** direction C_{60}'s stack with a separation between centers of a unit translation along **a**. This distance reduces from 9.9555 (10) to 9.9217 (13) to 9.8842 (12) Å in going from 157 to 93 to 13 K. Above the phase transition, disorder yields a myriad of ball-to-ball geometries. Below the phase transition there are two C_{60}'s in the asymmetric unit, and there are two distinct stacks. The changes in the *a* and *c* axes are primarily related to this partitioning of C_{60} molecules into two stacks that yields an ordered structure. There are two distinct stacking motifs, and these are illustrated in Fig. 3. Motif *A–A'* shows the closest contacts between the 'top' of Ball *A* and the 'bottom' of Ball A^i [(i) $1 + x, y, z$]. The intermolecular distances decrease as the temperature is lowered. At 93 K the distance between the planes C31/C32/C33/C48/C47/C46 and C7'/C8'/C24'/C23'/C22'/C21' is 3.313 (6) Å. The distance is 3.290 (12) Å at 13 K. The separation between the planes of the pentagons C65/C64/C77/C78/C79 and C102'/C103'/C104'/C116'/C117' is 3.224 (8) Å at 93 K and 3.206 (12) Å at 13 K. In Fig. 3 view *A–A'* depicts two pyracylene portions of C_{60}. The accepted view is that 6:6 ring junctions (C31/C32 and C22'/C23') are regions of greater electron density than 6:5 ring junctions. This is borne out by the much shorter bond distances of 6:6 ring junctions. The most important feature of the packing that is conserved is that the *A–A'* arrangement places the 6:6 ring junction of the neighboring ball above the center of the abutting hexagon. The inverse relationship also exists, giving rise to a cooperative intermolecular interaction. At 13 K the distance between the centroid of the C31/C32 bond and the centroid C7'/C8'/C24'/C23'/C22'/C21' of the abutting hexagon is 3.299 (5) Å. Similarly, the distance between the centroid of the C22'/C23' bond and the centroid of the C31/C32/C33/C48/C47/C46 hexagon is 3.306 (5) Å. In the case of the *B–B'* arrangement, we see another repetitive motif. Here, the inverse relationship places an atom above the centroid of an abutting pentagon. In Fig. 3 the C103' atom is 3.204 (8) Å above the centroid of C65/C64/C77/C78/C79, while C78 is 3.206 (8) Å above the centroid of C102'/C103'/C104'/C116'/C117'. The existence of these two van der Waals arrangements of coplanar faces can be expected to present a barrier to the rotational reorganization that characterizes the structures at high *T*.

Despite the ordering transition that yields two stacks of C_{60} molecules, some differences are evident in these stacks that persist even at 13 K. At 93 K the average equivalent isotropic displacement parameter for the atoms of the C_{60}'s is 0.025 (1) Å^2 for the *A* stack and 0.031 (1) Å^2 for the *B* stack. At 13 K these values are 0.024 (3) and 0.035 (3) Å^2. Unfortunately, different crystals were used for the measurements at 93 and 13 K, and some differences in crystallinity can account for the unexpected similarity in the U_{iso} values. However, at both temperatures, the difference in thermal motion between stacks *A* and *B* is correlated with differences in standard uncertainties for the metrical values for the two stacks, as depicted in Fig. 4 for the 93 K data. For ball *A*, the C—C bond lengths at the 6:6 ring junctions have an average value of 1.389 [3] and the C—C distances at the 6:5 ring junctions average 1.452 [3] Å (average deviations are given in square

brackets). The range of values is 1.382 (2)–1.395 (2) and 1.443 (2)–1.461 (2) Å. For ball *B* the corresponding values are 1.388 [5], 1.451 [5] Å, with ranges of 1.375 (2)–1.399 (3) and 1.434 (3)–1.467 (2) Å. Thus, while the average distances agree, a greater range exists for ball *B*, which retains more rotational disorder.

4. Discussion

Similar ordering transitions into two different stacks take place in other structures of solvates of [60]fullerene. One example is the solvate $2C_{60} \cdot 3CS_2$ which orders at 168 K (Olmstead *et al.*, 2000). In these structures one stack of C_{60}'s displays laterally shifted face-to-face contacts of coplanar hexagons, whereas the other stack contains laterally shifted
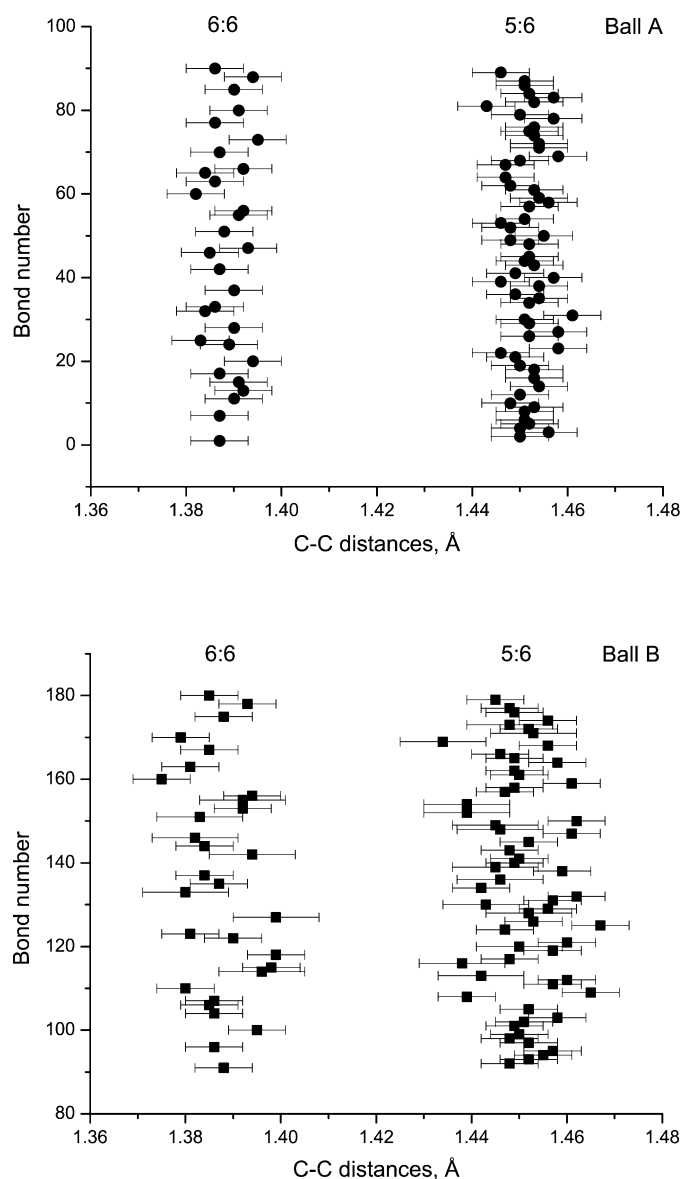

Figure 4
Plots of the two sets of 90 C—C distances for the two different stacks of C_{60} molecules at 93 K. Error bars are drawn at the 3σ level.

face-to-face stacks of coplanar pentagons. Upon closer examination, the first stacking motif is better described as a stack of pyracylene units and in the second case, a stack of corranulene units. Therefore, $C_{60}\cdot4$benzene and $2C_{60}\cdot3CS_2$ both order into the same two different kinds of stacks at low temperature. One difference is that the $C_{60}\cdot4$benzene transition is less sharp. We examined the differential scanning calorimetry (DSC) and could not detect a strong isotherm for $C_{60}\cdot4$benzene. Small energy changes are involved: for example, at 134 K the amount of thermal energy available is only 1.11 kJ mol^{-1}. One could imagine that the structure is passing through numerous stages as the crystal is cooled, beginning with a Boltzmann distribution of many preferred orientations with a rather flat potential energy surface, eventually reaching an energy landscape with two major disordered orientations, and ultimately the ordered structure at 134 K and below.

Do the two sets of co-planar faces represent van der Waals limits and are they energetically equal? X-ray crystallography cannot fully answer this question, but some information is available from an examination of the displacement parameters at different temperatures. In the title compound, the average displacement parameter for the pyracylene stack, labelled A–A', is consistently larger than the average displacement parameter of the corranulene stack, labelled B–B', even at the lowest temperature examined. Thus it would seem that the sharpening of the potential wells as the temperature is lowered is sufficient to cause partitioning into the two stacking motifs, but the one with hexagons facing hexagons is a deeper potential surface than that with pentagons facing pentagons.

Although a 13 K dataset was collected, a better crystal was used in the data collected at 93 K and, consequently, those values are more reliable. The range of C—C distances and average values are in line with those previously determined at 90 K for the ordered structure of $C_{60}\cdot$Pt(OEP)$\cdot2C_6H_6$ (Olmstead *et al.*, 2003), OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato, where the C—C bonds of 6:6 ring junctions averaged 1.387 [3] Å and the 6:5 ring junctions averaged 1.451 [3] Å.

Lastly, why was the ordered structure missed in earlier studies carried out below the transition temperature? It was missed because the superlattice reflections are much weaker than the primary reflections and because the unit cell was determined using a few reflections selected from a rotation photograph of a rather small crystal. With the use of modern CCD detectors the superlattice would have been obvious. Again, because of the poor quality of the 13 K crystal used in the study, the possibility of another order–disorder transition between 93 and 13 K cannot be ruled out.

References

Babu, V. S. & Seehra, M. S. (1992). *Chem. Phys. Lett.* **196**, 569–572.

Balch, A. L., Lee, J. W., Noll, B. C. & Olmstead, M. M. (1993). *J. Chem. Soc. Chem. Commun.* pp. 56–58.

Bruker (2002a). *SMART.* Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002b). *SAINT.* Bruker AXS Inc., Madison, Wisconsin, USA.

Bürgi, H. B., Blanc, E., Schwarzenbach, D., Liu, S., Lu, Y.-J., Kappes, M. M. & Ibers, J. A. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 640–643.

Bürgi, H. B., Restori, R., Schwarzenbach, D., Balch, A. L., Lee, J. W., Noll, B. C. & Olmstead, M. M. (1994). *Chem. Mater.* **6**, 1325–1329.

Heiney, P. A., Fischer, J. E., McGhie, A. R., Romanow, W. J., Denenstein, A. M., McCauley Jr, J. P., Smith, A. B. & Cox, D. E. (1991). *Phys. Rev. Lett.* **66**, 2911–2914.

Johnson, R. D., Yannoni, C. S., Dorn, H. C., Salem, J. R. & Bethune, D. S. (1992). *Science*, **255**, 1235–1238.

Krätschmer, W., Lamb, L. D., Fostiropoulos, K. & Huffman, D. R. (1990). *Nature*, **347**, 354–358.

Meidine, M. F., Hitchcock, P. B., Kroto, H. W., Taylor, R. & Walton, D. R. M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1534–1537.

Olmstead, M. M., de Bettencourt-Dias, A., Lee, H. M., Pham, D. & Balch, A. L. (2003). *Dalton Trans.* pp. 3227–3232.

Olmstead, M. M., Jiang, F. & Balch, A. L. (2000). *J. Chem. Soc. Chem. Commun.* pp. 483–484.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.