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Novel infinite three-dimensional network of neutral fullerene molecules in $(C_{60})_8$(twin-TDAS)$_6$

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The crystal structure of $(C_{60})_8$(twin-TDAS)$_6$ [twin-TDAS = $C_4S_6N_4$ = 3,3′,4,4′-tetrathiobis(1,2,5-thiadiazole)] has been redetermined at low temperature in the correct space group [$I23$, a = 18.849 (1) Å]. Structural analysis reveals a novel three-dimensional close-contact network of C_{60} molecules with tetrahedral holes similar to pristine C_{60}.

1. Introduction

The synthesis and X-ray study of $(C_{60})_8(C_4S_6N_4)_6$, octa([60]-fullerene)hexa[3,3′,4,4′-tetrathiobis(1,2,5-thiadiazole)], was published some years ago by two of us and collaborators (Kotov *et al.*, 1994). Some ambiguities remained, however, and prompted us to reexamine the crystal structure. We report here on the full structural resolution in the correct space group ($I2_3$). An in-depth study of the crystal architecture reveals a novel, extended, three-dimensional network of polyhedral clusters $(C_{60})_8$. After the successful doping of solid C_{60} with alkali and alkaline earth metals (Rosseinsky, 1998), new structural types of C_{60} solids with electronic properties were discovered with polymeric C_{60} salts such as A_1C_{60} (A = K, Rb, Cs; Pekker *et al.*, 1994) and Na_2RbC_{60} (Rosseinsky *et al.*, 1992). In the on-going search for new C_{60} supramolecular architectures, another type of C_{60} network, stabilized by $N-H\cdots\pi$ interactions has recently been reported (Fowkes *et al.*, 1997).

The crystal structure was originally described in the orthorhombic space group $I222$ with parameters a = 19.007 (8), b = 19.024 (9) and c = 18.991 (7) Å (Kotov *et al.*, 1994). Interatomic distances within C_{60} ranged from 1.09 (3) to 1.49 (3) Å for 6,6 bonds and from 1.31 to 1.67 Å for 5,6 bonds, to be compared with standard values of 1.40 and 1.46 Å for neutral C_{60} (Dresselhaus *et al.*, 1996). Buckyball diameters ranged from 6.90 to 7.12 Å. These abnormally wide distributions of values prompted us to reconsider the space-group assignment, considering cubic symmetry. However, structural resolution in cubic symmetry at room temperature did not significantly improve the data, owing to high vibrations of the fullerene C atoms. Thus, new data were collected at low temperature (100 K).

2. Experimental

Single crystals of the title compound were grown according to Kotov *et al.* (1994) and measured on a Stoe imaging plate equipped with a cold nitrogen stream. Careful examination of the data allowed an unambiguous assignment of the cubic

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{504}N_{24}S_{36}$
Chemical formula weight	7543.44
Cell setting	Cubic
Space group	*I*23
a, *b*, *c* (Å)	18.8492 (10)
V (Å^3)	6697.0 (6)
Z	1
D_x (Mg m^{-3})	1.870
Radiation type	Mo *Kα*
Wavelength (Å)	0.71073
No. of reflections for cell parameters	5000
θ range (°)	1.45–25.15
μ (mm^{-1})	0.380
Temperature (K)	100 (2)
Crystal form	Plate-like
Crystal size (mm)	0.37 × 0.27 × 0.23
Crystal colour	Black
Data collection	
Diffractometer	Stoe IPDS
Data collection method	Rotation, $\Delta\varphi = 1.2°$ scans
Absorption correction	*ABSCOR* (Stoe & Cie, 1996)
$T_{\min}$	0.871
$T_{\max}$	0.916
No. of measured reflections	12 851
No. of independent reflections	1764
No. of observed reflections	1243
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.0143
$\theta_{\max}$ (°)	25.15
Range of *h*, *k*, *l*	$-14 \rightarrow h \rightarrow 14$
	$0 \rightarrow k \rightarrow 15$
	$2 \rightarrow l \rightarrow 21$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0456
$wR(F^2)$	0.1045
S	0.613
No. of reflections used in refinement	1764
No. of parameters used	213
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1321P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.456
$\Delta\rho_{\min}$ (e Å^{-3})	−0.224
Extinction method	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection	*EXPOSE* (Stoe & Cie, 1996)
Cell refinement	*SELECT* (Stoe & Cie, 1996)
Data reduction	*INTEGRATE* (Stoe & Cie, 1996)
Structure solution	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*SHELXL*97 (Sheldrick, 1997)

Laue symmetry $m\bar{3}$ and the structure was successfully resolved in the space group *I*23. The number of Friedel pairs of reflections was 790. Experimental details are given in Table 1.[1]

3. Results

3.1. Crystal packing

The asymmetric unit is comprised of one fourth of a twin-TDAS [twin-TDAS = $C_4S_6N_4$ = 3,3′,4,4′-tetrathiobis(1,2,5-thiadiazole)] molecule (situated on a site with 222 symmetry) and one third of a C_{60} molecule (situated on a threefold axis). The unit cell is shown in Fig. 1. To better understand the crystal architecture, the best way is to focus on the C_{60} packing. One can view the structure as a cubic (*I*-centred) network of $(C_{60})_4$ tetrahedra (Fig. 2). An apex of one such (inner) tetrahedron (centred at say 0,0,0) is in close contact with the three C_{60}'s forming a face of the neighbouring tetrahedron centred at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. These close contacts thus form four new (outer) tetrahedra around each inner tetrahedron leading to interconnected $(C_{60})_8$ clusters (Fig. 3). The inner tetrahedra are regular, with sides of 10.055 Å (centre-to-centre distance), whereas the outer ones (sharing three sides of 10.055 Å with the inner tetrahedra) have three extra sides of length 9.977 Å. The resulting assembly of five tetrahedra is a polyhedron (one per unit cell) and, in fact, a member of the infinite family of concave deltahedra, polyhedra bordered by triangular faces. It is called an omnicapped tetrahedron (Fig. 4*a*) and bears two different types of apices: six-coordinated (the four apices of the core tetrahedron) and three-coordinated (the outer four). In the crystal structure of $(C_{60})_8(C_4S_6N_4)_6$, a six-coordinated apex of one omnicapped tetrahedron is a three-coordinated apex of the neighbouring one. Thus, all C_{60} sites are equivalent. Empty spaces are found in between those $(C_{60})_8$ clusters which are occupied by TDAS molecules (centres of the unit cell faces and edges, Fig. 1).

Are there sites available for doping? $(C_{60})_8(C_4S_6N_4)_6$ is composed of tetrahedra of C_{60}, so naturally, akin to pristine C_{60}, there are sites available for doping. Two types are readily identified. Site *A* (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) is formed by the central regular

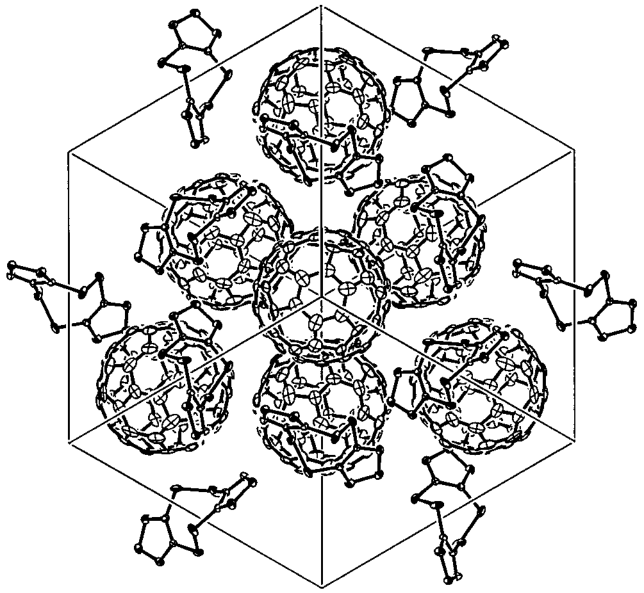

Figure 1
Projection of the unit cell along the [111] direction.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF0010). Services for accessing these data are described at the back of the journal.

tetrahedron. Site *B* (at 0.6235, 0.6235, 0.6235) is pseudotetrahedral: it is formed by the four outer tetrahedra of the omnicapped tetrahedron. Sites *A* and *B* are of slightly different size, with respective radii of 1.16 and 1.13 Å, yielding a 8% difference in volume. Stoichiometries are extremely interesting: there are one *A* site and four *B* sites per $(C_{60})_8$ cluster. Therefore, even full occupation of all sites would not lead to a formal charge of 1−, but 0.625−, opening the way to mixed-valence fulleride salts.

3.2. Molecular structures

Twin-TDAS is represented in Fig. 5. The angle between the two SN_2C_2 rings is 48.45 (15)°. The numbering scheme and vibration ellipsoids for C_{60} are shown in Fig. 6. Interatomic parameters now have the usual values [diameters: min = 7.051, max = 7.085, av. = 7.07 (1) Å, *d*(6,6): min = 1.32 (1), max = 1.43 (1), av. = 1.37 (4) Å, *d*(5,6): min = 1.40 (1), max = 1.52 (1), av. = 1.46 (4) Å]. Vibration ellipsoids have a disk-like shape oriented tangentially to the C_{60} surface. Given the shape of the fullerene molecule, these ellipsoids intuitively reflect the local atomic motions and indeed they have come to be an indication of a well behaved fullerene structure.

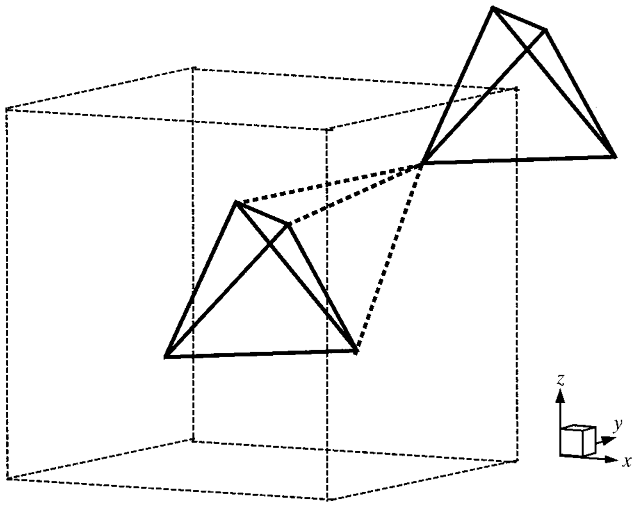

Figure 2
Inner (solid lines) and outer tetrahedra (dashed lines). For the sake of clarity, only two inner tetrahedra are shown and the outer one linking them.

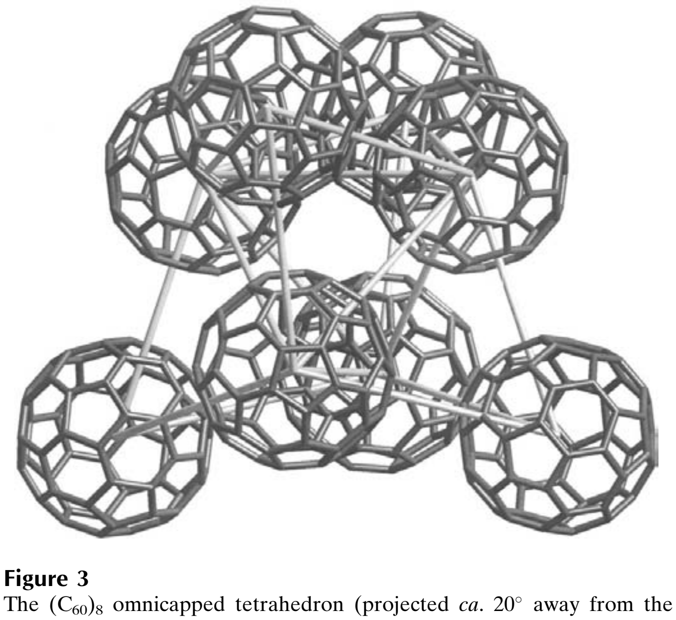

Figure 3
The $(C_{60})_8$ omnicapped tetrahedron (projected *ca*. 20° away from the [110] direction).

3.3. Intermolecular interactions

C_{60}–C_{60} interactions are of the type bond(5,6)-over-hexagon with short distances ranging from 3.31 to 3.63 Å. Twin-TDAS/C_{60} interactions show a neat key-to-the-lock packing and involve mainly one bond on each molecule crossing at right angles (C12—C16 and N1—S1) with distances ranging from 3.547 (6) to 3.577 (7) Å. The shortest contact between twin-TDAS molecules is S1—S2 [3.677 (6) Å].

4. Discussion

The prototypical neutral fullerene matrix is, of course, C_{60} itself. Doping of this neutral matrix with alkali and alkaline-earth metals has led to a large, albeit limited, number of compounds (Rosseinsky, 1998). $(C_{60})_8(C_4S_6N_4)_6$ is another example of a neutral fullerene matrix. In the latter, it is useful to consider as the basic unit not C_{60}, but the omnicapped tetrahedron $(C_{60})_8$. The problem of the densest packing of *n* (finite) spheres is not trivial. Sloane *et al.* (1995), using the criterion of minimal second moment, showed that, for *n* = 8,

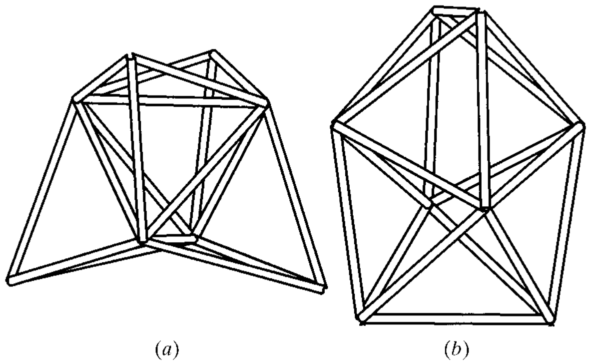

Figure 4
(*a*) Omnicapped tetrahedron; (*b*) snub disphenoid.

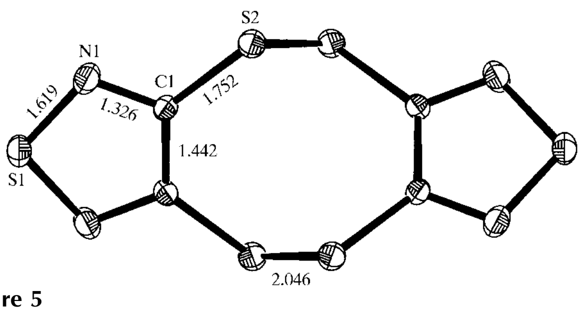

Figure 5
Twin-TDAS numbering scheme, vibration ellipsoids and bond distances.

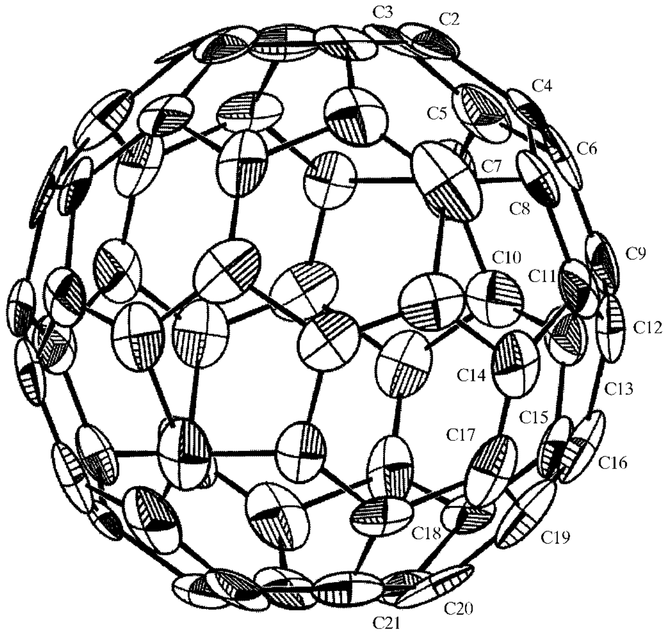

Figure 6
C_{60} numbering scheme and vibration ellipsoids.

the solution is the (convex) snub disphenoid (Fig. 4*b*, $V = 0.86l^3$, where l is the edge length). The omnicapped tetrahedron (Fig. 4*a*) present in $(C_{60})_8(C_4S_6N_4)_6$ is a concave solution ($V = 0.59l^3$). Packing forces, or the key-to-the lock principle of Kitaigorodsky (1984), are surely responsible for the observation of the latter rather than the former. We are thus in the presence of a three-dimensional network of nanoclusters of C_{60} molecules, showing that the first condition for cooperative properties (extended network of C_{60}'s in contact) can be fulfilled in neutral mixed crystals of fullerenes.

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References

Dresselhaus, M. S., Dresselhaus, G. & Eklund, P. C. (1996). *Science of Fullerenes and Carbon Nanotubes*, p. 60. New York: Academic Press.

Fowkes, A. J., Fox, J. M., Henry, P. F., Heyes, S. J. & Rosseinsky, M. J. (1997). *J. Am. Chem. Soc.* **119**, 10413–10423.

Kitaigorodsky, A. I. (1984). *Mixed Crystals*, Springer Series in Solid State Sciences 33. Berlin: Springer-Verlag.

Kotov, A. I., Konovalikhin, S. V., Pisarev, R. V., Shilov, G. V., Dyachenko, O. A. & Yagubskii, E. B. (1994). *Mendeleev Commun.* pp. 180–182.

Pekker, S., Jánossy, A., Mihaly, L., Chauvet, O., Carrard, M. & Forró, L. (1994). *Science*, **265**, 1077–1078.

Rosseinsky, M. J. (1998). *Chem. Mater.* **10**, 2665–2685.

Rosseinsky, M. J., Murphy, D. W., Fleming, R. M., Tycko, R., Ramirez, A. P., Siegrist, T., Dabbagh, G. & Barret, S. E. (1992). *Nature*, **356**, 416–418.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sloane, N. J. A., Hardin, R. H., Duff, T. D. S. & Conway, J. H. (1995). *Discrete Comput. Geom.* **14**, 237–259.

Stoe & Cie (1996). *STOE IPDS Software*, Version 2.75. Stoe & Cie, Darmstadt, Germany.