A single crystal X-ray diffraction study of a fully ordered cocrystal of pristine $Sc_3N@D_{3h}(5)$–C_{78}

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ABSTRACT

Black crystals of $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene) contain a fully ordered endohedral fullerene cage and fully ordered contents. Thus, the X-ray crystallographic study allows detailed examination of its structural properties. The planar Sc_3N group lies perpendicular to the threefold axis of the fullerene cage with the scandium ions bound to the three 6:6 ring junctions that lie in the horizontal mirror plane of the molecule. The Sc–N distances are 2.0111(10), 2.0106(10), and 1.9998(10) Å and the shortest Sc–C distances fall in the range 2.2371(13)–2.2591(13) Å. Those six carbon atoms nearest the scandium ions are the most pyramidalized carbon atoms in the molecule with an average $\theta_p = 13.9°$ compared to $\theta_p = 11.6°$ for C_{60} and to average $\theta_p = 11.3°$ for the 12 carbon atoms along the C_3 axis at the poles of the molecule. The C–C bond distances at the 6:6 and 5:6 ring junctions do not show the distinct variations that are found in C_{60}. The shortest average C–C bond length, 1.391(2) Å, and the longest average bond length, 1.466(1) Å, occur at 6:6 ring junctions.

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1. Introduction

Fullerenes and endohedral fullerenes are nearly spherical molecules with a clearly differentiated inner and outer surfaces. They have potential uses as electron acceptors in solar cells [1] and as contrast agents for magnetic resonance imaging [2]. For fullerenes and endohedral fullerenes, their high symmetry and smooth outer surface, which is made up of similarly sized pentagons and hexagons, produces crystals that are prone to disorder [3–5]. Cocrystallization of fullerenes with a metalloporphyrin such as Ni^{II}(OEP) or Co^{II}(OEP) has been shown to produce crystals with sufficient order to allow structure determination by single crystal X-ray diffraction [6]. $Sc_3N@I_h$–C_{80} was the first endohedral fullerene to be characterized by X-ray diffraction [7]. The process employed the cocrystal $Sc_3N@I_h$–C_{80}·Co^{II}(OEP)·1.5CHCl$_3$·0.5C$_6$H$_6$. $Sc_3N@I_h$–C_{80} is also the third most-abundant fullerene; only C_{60} and C_{70} are more abundant. The isolation and characterization of $Sc_3N@I_h$–C_{80} led to the discovery of many new molecules of the type $M_3N@C_{2n}$ that could incorporate a variety of trivalent metals including Sc, Y, Gd, Tb, Tm, and Lu, and a range of different cage sizes [8,9]. The process by which $Sc_3N@I_h$–C_{80} was made also produced its isomer $Sc_3N@D_{5h}$–C_{80} [10], as well as $Sc_3N@D_{3h}(5)$–C_{78} [11], and $Sc_3N@D_3(6140)$–C_{68} [12], each of which has been characterized crystallographically.

The initial characterization of $Sc_3N@D_{3h}(5)$–C_{78} also utilized the cocrystallization process [8]. However, crystals of $Sc_3N@D_{3h}(5)$–C_{78}·Co^{II}(OEP)·1.5(C$_6$H$_6$)·0.3(CHCl$_3$) were disordered. There are five possible IPR isomers for the C_{78} cage [13]. Although it was possible to determine that $D_{3h}(5)$–C_{78} cage was present from the crystallographic data, three orientations of the cage and three orientations of the Sc_3N unit were present. Of necessity, the first refinement used a rigid model for the fullerene cage. Subsequently, the crystallographic data were re-refined and improved using a computed model that resulted from density functional calculations [14]. While these studies provided clear evidence about the basic structure of $Sc_3N@D_{3h}(5)$–C_{78}, the crystallographic disorder precluded detailed analysis of the bond parameters within this molecule. The structure of an adduct of $Sc_3N@D_{3h}(5)$–C_{78} formed by the Prato reaction has been crystallographically characterized [15]. Since functionalization can distort the shape of fullerene cages and alter the placement of metal ions within endohedral fullerenes [16,17], it is important to have structural studies of intact, pristine fullerenes.

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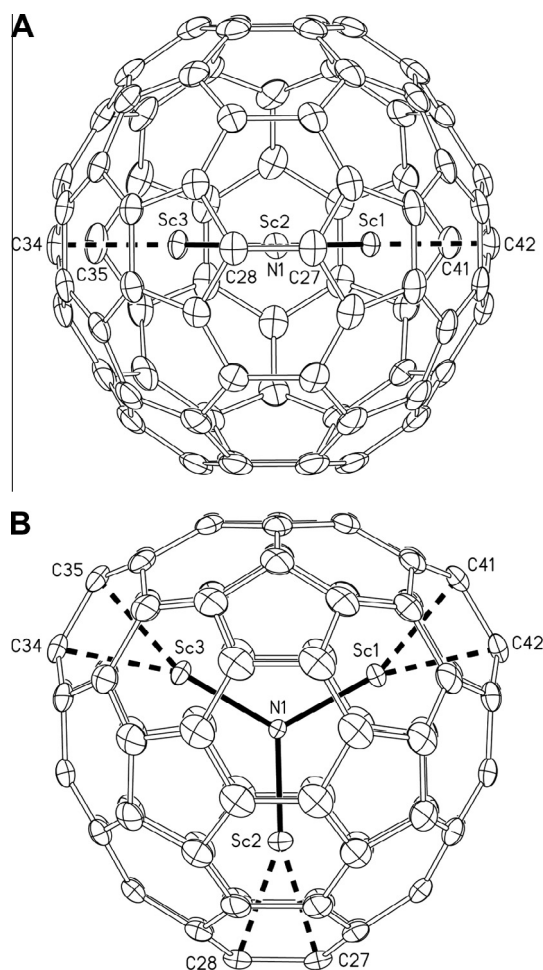
Fig. 1. Two orthogonal views of Sc$_3$N@D_{3h}(5)–C$_{78}$ with the displacement parameters at the 50% probability level. In orientation (A), the threefold axis is vertical and the view is down one of the three, twofold axes. The orientation in (B) looks down the threefold axis. The shortest Sc–C contacts are shown.
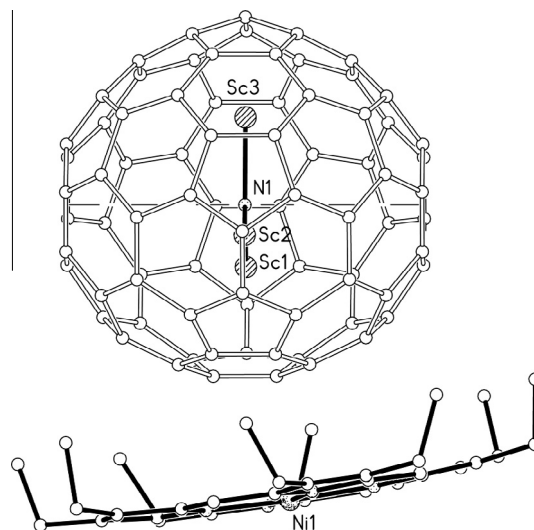
Fig. 2. A drawing showing the interaction between the fullerene and porphyrin in Sc$_3$N@D_{3h}(5)–C$_{78}$·Ni^{II}(OEP)·3(benzene) with arbitrarily sized circles for the atoms. For clarity, the benzene molecules and the hydrogen atoms have been omitted. The threefold axis of the cage is indicated by the horizontal dashed line and the horizontal mirror plane of the cage is aligned vertically.

Fig. 3. A drawing D_{3h}(5)–C$_{78}$ showing the eight types of carbon atoms labeled a–h. (Color online.)

Table 1
Selected bond lengths (Å) and angles (°) for Sc$_3$N@D_{3h}(5)–C$_{78}$·Ni^{II}(OEP)·2(benzene).

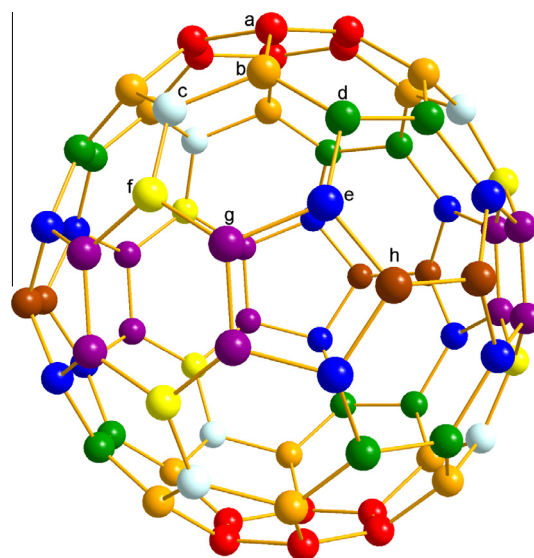|	
Sc(1)–N(1)	2.0111(10)
Sc(1)–C(42)	2.2371(13)
Sc(1)–C(41)	2.2591(13)
Sc(2)–N(1)	2.0106(10)
Sc(2)–C(27)	2.2394(13)
Sc(2)–C(28)	2.2565(13)
Sc(3)–N(1)	1.9998(10)
Sc(3)–C(35)	2.2498(14)
Sc(3)–C(34)	2.2514(14)
Sc(3)–N(1)–Sc(2)	121.58(5)
Sc(3)–N(1)–Sc(1)	121.36(5)
Sc(2)–N(1)–Sc(1)	117.06(5)
ΣSc–N–Sc angles	360.00

Here we report the formation and structural analysis of a remarkably well-ordered cocrystal formed from Sc$_3$N@D_{3h}(5)–C$_{78}$ that allows us to examine details of the structure of this endohedral fullerene in pristine form.

2. Results

Black crystals of Sc$_3$N@D_{3h}(5)–C$_{78}$·Ni^{II}(OEP)·2(benzene) were grown through the diffusion of a solution of Sc$_3$N@D_{3h}(5)–C$_{78}$ in benzene into a benzene solution of Ni^{II}(OEP). Crystal data are given in the Section 4. The crystal is fully ordered with one molecule of Sc$_3$N@D_{3h}(5)–C$_{78,}$ one molecule of Ni^{II}(OEP), and one molecule of benzene in general positions and two half molecules of benzene in special positions on twofold axes in the space group $C2/c$.

Fig. 1 shows two orthogonal drawings of the Sc$_3$N@D_{3h}(5)–C$_{78}$ molecule. As seen in part A, the molecule has a slightly nanotubular shape that is related to the structures of C$_{70}$, D_{5h}(1)–C$_{90}$, La$_2$@D_5(450)–C$_{100}$, and Sm$_2$@D_{3d}(822)–C$_{104}$ [18–20]. The length of the nanotube as measured by the distance between the centers of the hexagons along the threefold axis at opposite ends of the molecule is 7.948 Å. The widths of the molecule, as defined by the distances between the centers of the C–C bonds nearest the three scandium ions and the centers of the opposite hexagons, are: 7.784, 7.811, and 7.812 Å. As found previously, the Sc$_3$N unit
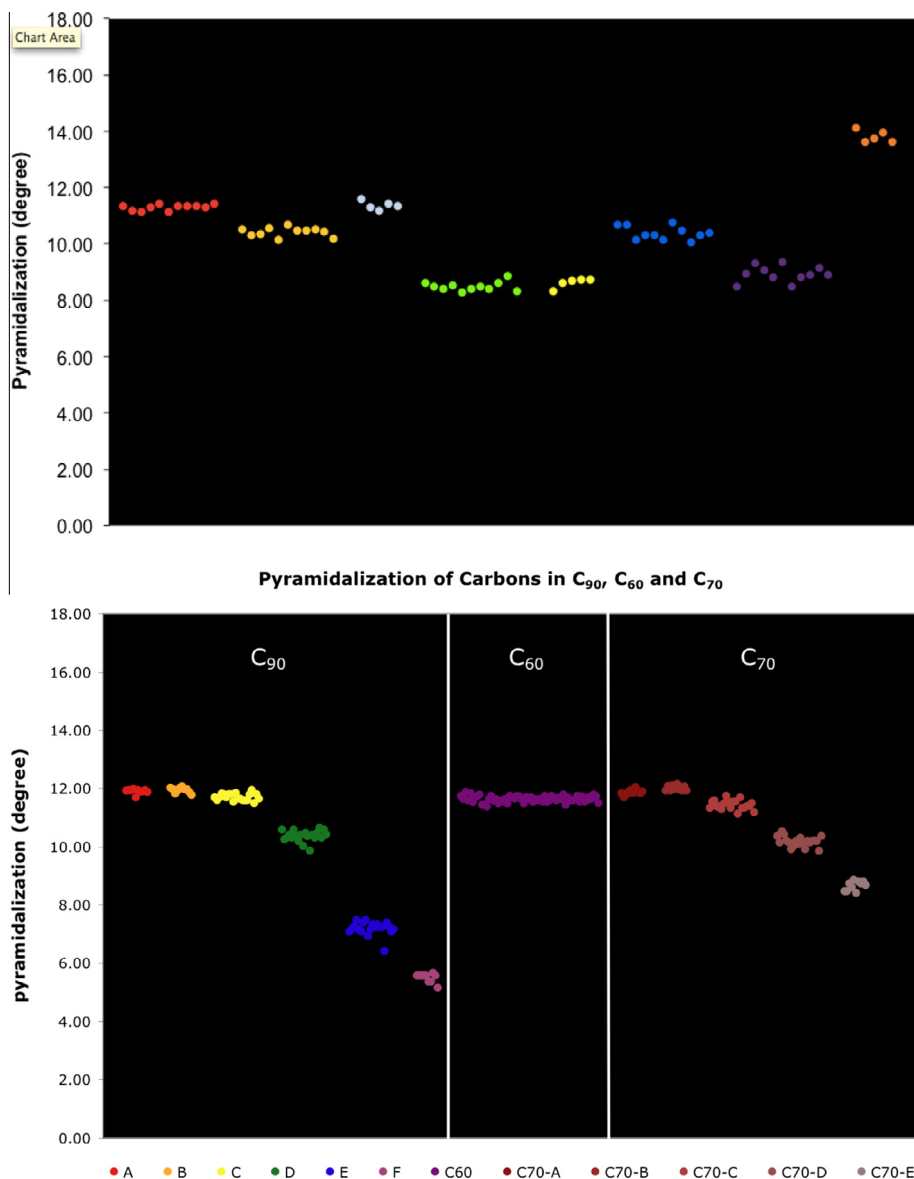
Fig. 4. Graphs comparing the pyramidalization of the carbon atoms in $Sc_3N@D_{3h}(5)–C_{78}$ (top) with those in C_{90}, C_{60} and C_{70} (bottom from Ref. [16]). The color coding for $Sc_3N@D_{3h}(5)–C_{78}$ follows that in Fig. 3. (Color online.)

is planar and lies perpendicular to the threefold axis of the fullerene cage. Selective bond distances and angles related to the Sc_3N unit are given in Table 1. The deviations from the least squares plane of the Sc_3N unit are: N1, −0.0070(8); Sc1, 0.0023(3); Sc2, 0.0023(3); Sc3, 0.0024(3). The Sc–N distances are similar and fall in the range 1.9998(10)–2.0111(10) Å. For comparison, the computed Sc–N distance from the earlier density functional study was 1.997 Å [12]. Additionally, the Sc–N distances in the Prato adduct $Sc_3N@D_{3h}(5)–C_{78}$-$(CH_2)_2NC(C_6H_5)_3$ are also similar: 2.001(2), Sc2–N1 1.999(2), and 2.001(2) Å [13]. The calculated Sc–C distance from the density functional study was 2.255 Å, whereas the experimental Sc–C distances (to the nearest carbon atoms) range from 2.2371(13) to 2.2591(13) Å for $Sc_3N@D_{3h}(5)–C_{78}·Ni^{II}(OEP)·2$(benzene) and from 2.210(3) to 2.271(3) Å for the Prato adduct.

Fig. 2 shows the relative orientations of the $Sc_3N@D_{3h}(5)–C_{78}$ and $Ni^{II}(OEP)$ molecules in $Sc_3N@D_{3h}(5)–C_{78}·Ni^{II}(OEP)·2$(benzene). The Sc_3N unit is arranged so that it is nearly perpendicular to the plane of the porphyrin. The angle between the normal to the porphyrin plane and the normal to the Sc_3N plane is 81.13(1)°. Similar orientations of M_3N units have been seen in cocrystals

of $Ni^{II}(OEP)$ with a number of molecules of the type $M_3N@I_h$$–C_{80}$ [21]. The shortest contact between the nickel ion in the porphyrin and a carbon atom in the adjacent fullerene is 2.8773(13) Å. Such short contacts are characteristic of cocrystals formed from fullerenes or endohedral fullerenes and metalloporphyrins [4,5,9,10].

There are eight different types of carbon atoms in $Sc_3N@D_{3h}(5)–$$C_{78}$. Fig. 3 shows a drawing of the $D_{3h}(5)–C_{78}$ molecule with these eight different types of carbon atoms labeled a–h. Fig. 4 shows the pyramidalization angles θ_p [22], (θ_p for graphite = 0°; θ_p for C_{60} = 11.6°) of the carbon atoms in $Sc_3N@D_{3h}(5)–C_{78}$. For the nanotubular molecules C_{70} and C_{90}, the pyramidalization angles generally decrease as one moves from the poles of the molecule along the principle symmetry axis onto the waist of the molecule. A somewhat similar trend is seen for $Sc_3N@D_{3h}(5)–C_{78}$, but at the waist, the g-type of carbon atoms have the largest pyramidalization of any type of carbon atoms in the molecule. This situation is not surprising, since the g-type carbon atoms are the atoms closest to the scandium ions and such carbon atoms are usually the most pyramidalized in endohedral fullerenes [23–25].
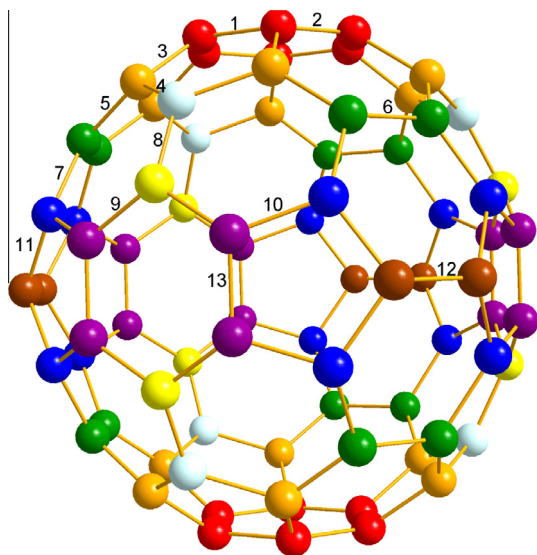
Fig. 5. A drawing $D_{3h}(5)$–C_{78} showing the 13 types of C–C bonds labeled 1–13.

Table 2
Average C–C bond lengths (in Å) for $Sc_3N@D_{3h}(5)$–C_{78}.

6:6 bonds						
2 a–a	5 b–d	6 d–d	7 d–e	8 c–f	9 f–g	12 h–h
1.400(4)	1.424(3)	1.466(1)	1.453(2)	1.391(2)	1.434(2)	1.444(1)
5:6 bonds						
1 a–a	3 a–b	4 b–c	10 e–g	11 e–h	13 g–g	
1.441(4)	1.434(4)	1.454(4)	1.444(2)	1.452(3)	1.421(4)	

Within the $D_{3h}(5)$–C_{78} cage, there are 13 types of C–C bonds, whose locations can be seen by turning to Fig. 5. Table 2 gives the average C–C distances for these 13 types of bonds. In C_{60} the C–C bonds at 6:5 and 6:6 ring junctions differ in length. Those at 6:6 ring junctions are short, 1.383(4) Å, while those at the 5:6 junctions are longer, 1.453(5) Å [26]. In contrast, in $Sc_3N@D_{3h}(5)$–C_{78} the situation is quite different. The c–f (8) bonds are on average the shortest C–C bonds (bond length, 1.391(2) Å) in the molecule, while the d–d (6) bonds are the longest (average bond length, 1.466(1) Å). Both of these occur at 6:6 ring junctions. In contrast the range of C–C distances at the 5:6 ring junctions is smaller: from 1.434(4) Å for the a–b (3) bonds to only 1.454(4) Å for the b–c (4) bonds. The average C–C distance for the carbon atoms nearest the scandium ions does not appear exceptional: g–g (13), 1.421(4) Å.

3. Discussion

This study has provided detailed structural information for the endohedral fullerene $Sc_3N@D_{3h}(5)$. In the black crystals of $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene) the fullerene cage and its contents are fully ordered, whereas crystals of $Sc_3N@D_{3h}(5)$–C_{78}·Co^{II}(OEP)·1.5(C_6H_6)·0.3(CHCl$_3$) displayed three different orientations of the cage and of the Sc_3N unit. Likely factors responsible for the differences in internal order in these two crystals include the purity of the endohedral fullerene sample and the difference in solvents used for crystallization that resulted in the formation of different solvates. Comparison of the structure of pristine $Sc_3N@D_{3h}(5)$–C_{78} in $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene) with that of functionalized $Sc_3N@D_{3h}(5)$–C_{78} in the Prato adduct $Sc_3N@D_{3h}(5)$–C_{78}–$(CH_2)_2NC(C_6H_5)_3$ [13] reveals that functionalization does not influence the location of the Sc_3N unit within the fullerene cage but does cause a local distortion where addition occurs.

4. Experimental

4.1. Crystal growth

A sample of $Sc_3N@D_{3h}(5)$ was obtained from electric arc generated soot formed from cored graphite rods and filled with scandium(III) oxide and purified by standard techniques utilized previously [11,15]. Black crystals of $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene) were obtained by the slow diffusion of solutions of $Sc_3N@D_{3h}(5)$–C_{78} dissolved in benzene and of Ni^{II}(OEP) also in benzene.

4.2. Crystal structure determination

A black crystal of $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene) was mounted in the nitrogen cold stream on the goniometer head of a Rigaku Crystal-Logic Kappa diffractometer equipped with a Saturn 724+ detector. Data were collected with the use of synchrotron radiation ($\lambda = 0.68890$ Å) at Beamline I19 of the Diamond Light Source and processed using the program CRYSTALCLEAR [27]. The structure was solved by direct methods (SHELXS97) and refined by full-matrix least-squares on F^2 (SHELXL97) [28].

4.3. Crystal data for $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene)

$C_{126}H_{56}N_5NiSc_3$: $M = 1833.35$, black parallelepiped $0.08 \times 0.03 \times 0.02$ mm, $\lambda = 0.68890$ Å, monoclinic, space group $C2/c$, $a = 25.3346(19)$, $b = 14.8858(11)$, $c = 39.243(3)$ Å, $\beta = 93.448(2)°$, $T = 120(2)$ K, $V = 14772.6(19)$ Å^3, $Z = 8$, 57 792 reflections collected, 24 117 unique ($R_{int} = 0.031$) which were used in all calculations; $2\theta_{max} = 63.32°$; minimum/maximum transmission = 0.955/0.998 (multi-scan absorption correction applied). The final $wR(F_2)$ was 0.123 (all data), conventional $R_1 = 0.041$ computed for 22 468 reflections with $I > 2\sigma(I)$, 1224 parameters and 0 restraints.

Appendix A. Supplementary material

CCDC 891126 contains the supplementary crystallographic data for $Sc_3N@D_{3h}(5)$–C_{78}·Ni^{II}(OEP)·2(benzene). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article, which show the C_{78} numbering scheme as well as details of the pyramidalization (POAV) calculation, can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.035.

References

[1] M. Rudolf, S. Wolfrum, D.M. Guldi, L. Feng, T. Tsuchiya, T. Akasaka, L. Echegoyen, Chem. Eur. J. 13 (2012) 5136.
[2] M. Mikawa, H. Kato, M. Okumura, M. Narazaki, Y. Kanazawa, N. Miwa, H. Shinohara, Bioconjugate Chem. 12 (2001) 510.
[3] M.M. Olmstead, A.L. Balch, H.M. Lee, Acta Crystallogr., Sect. B 68 (2012) 66.
[4] H.B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-J. Lu, M.M. Kappes, J.A. Ibers, Angew. Chem., Int. Ed. 31 (1992) 640.
[5] P.A. Heiney, J.E. Fischer, A.R. McGhie, W.J. Romanow, A.M. Denenstein, J.P. McCauley, A.B. Smith Jr., D.E. Cox, Phys. Rev. Lett. 66 (1991) 2911.

[6] M.M. Olmstead, D.A. Costa, K. Maitra, B.C. Noll, S.L. Phillips, P.M. Van Calcar, A.L. Balch, J. Am. Chem. Soc. 121 (1999) 7090.

[7] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M.R. Jordan, J. Craft, E. Hadju, R. Bible, M.M. Olmstead, K. Maitra, A.J. Fisher, A.L. Balch, H.C. Dorn, Nature 401 (1999) 55.

[8] M.M. Olmstead, A.L. Balch, J.R. Pinzón, L. Echegoyen, H.W. Gibson, H.C. Dorn, in: T. Akasaka, F. Wudl, S. Nagase (Eds.), Chemistry of Nanocarbons, John Wiley & Sons, Ltd., Singapore, 2010, p. 239.

[9] L. Dunsch, S.-F. Yang, Small 3 (2007) 1298.

[10] T. Cai, L. Xu, M.R. Anderson, Z. Ge, T. Zuo, X. Wang, M.M. Olmstead, A.L. Balch, H.W. Gibson, H.C. Dorn, J. Am. Chem. Soc. 128 (2006) 8581.

[11] M.M. Olmstead, A. de Bettencourt-Dias, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A.L. Balch, Angew. Chem., Int. Ed. 40 (2001) 1223.

[12] M.M. Olmstead, H.M. Lee, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A.L. Balch, Angew. Chem., Int. Ed. 42 (2003) 900.

[13] P.W. Fowler, D.E. Manolopoulous, An Atlas of Fullerenes, Clarendon, Oxford, 1995.

[14] J.M. Campanera, C. Bo, M.M. Olmstead, A.L. Balch, J.M. Poblet, J. Phys. Chem. A 106 (2002) 12356.

[15] T. Cai, L. Xu, H.W. Gibson, H.C. Dorn, C.J. Chancellor, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 129 (2007) 10795.

[16] G.-W. Wang, T.-X. Liu, M. Jiao, N. Wang, S.-E. Zhu, C. Chen, S.-F. Yang, F.L. Bowles, C.M. Beavers, M.M. Olmstead, B.Q. Mercado, A.L. Balch, Angew. Chem., Int. Ed. 50 (2011) 4658.

[17] O. Lukoyanova, C.M. Cardona, J. Rivera, L.Z. Lugo-Morales, C.J. Chancellor, M.M. Olmstead, A. Rodriguez-Fortea, J.M. Poblet, A.L. Balch, L. Echegoyen, J. Am. Chem. Soc. 129 (2007) 10423.

[18] H. Yang, C.M. Beavers, Z. Wang, A. Jiang, Z. Liu, H. Jin, B.Q. Mercado, M.M. Olmstead, A.L. Balch, Angew. Chem., Int. Ed. 49 (2010) 886.

[19] C.M. Beavers, H. Jin, H. Yang, Z. Wang, X. Wang, H. Ge, Z. Liu, B.Q. Mercado, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 133 (2011) 15338.

[20] B.Q. Mercado, A. Jiang, H. Yang, Z. Wang, H. Jin, Z. Liu, M.M. Olmstead, A.L. Balch, Angew. Chem., Int. Ed. 48 (2009) 9114.

[21] S. Stevenson, C.J. Chancellor, H.M. Lee, M.M. Olmstead, A.L. Balch, Inorg. Chem. 47 (2008) 1420.

[22] R.C. Haddon, L.T. Scott, Pure Appl. Chem. 58 (1986) 137.

[23] H.M. Lee, M.M. Olmstead, E. Iezzi, J.C. Duchamp, H.C. Dorn, A.L. Balch, J. Am. Chem. Soc. 124 (2002) 3494.

[24] L. Echegoyen, C.J. Chancellor, C.M. Cardona, B. Elliott, J. Rivera, M.M. Olmstead, A.L. Balch, Chem. Commun. (2006) 2653.

[25] T. Zuo, C.M. Beavers, J.C. Duchamp, A. Campbell, H.C. Dorn, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 129 (2007) 2035.

[26] M. Fedurco, M.M. Olmstead, W.R. Fawcett, Inorg. Chem. 34 (1995) 390.

[27] Rigaku Americas and Rigaku Corporation, CRYSTALCLEAR (Version 2.0), Rigaku Americas, 9009 TX, USA 77381-5209, 2009.

[28] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.