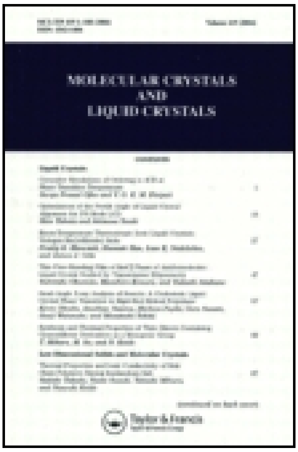

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Local Bond Structure of Yttrium in the Metallofullerene YC82

Yasushi Tomioka [a], Hiroshi Kajiyama [a] [b], Masayoshi Ishibashi [a] & Yoshio Taniguchi [a]

[a] Advanced Research Laboratory, Hitachi, Ltd., Hatoyama, Saitama, 350-03, Japan

[b] Joint Research Center for Atom Technology (JRCAT) c/o National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki, 305, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Yasushi Tomioka , Hiroshi Kajiyama , Masayoshi Ishibashi & Yoshio Taniguchi (1995): Local Bond Structure of Yttrium in the Metallofullerene YC82, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 347-352

To link to this article: http://dx.doi.org/10.1080/10587259508034015

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 347–352
Reprints available directly from the publisher
Photocopying permitted by license only

LOCAL BOND STRUCTURE OF YTTRIUM IN THE METALLOFULLERENE YC82

YASUSHI TOMIOKA, HIROSHI KAJIYAMA*, MASAYOSHI ISHIBASHI, AND YOSHIO TANIGUCHI
Advanced Research Laboratory, Hitachi, Ltd., Hatoyama Saitama, 350-03, Japan

Abstract Extended X-ray absorption fine structure measurement was performed using the sample containing only YC82 as a metallofullerene. The spectrum measured on the K-edge of the Y showed that a Y atom has two neighboring carbons at distance of 2.41Å. This suggests that the Y atom is located on the double bond of the carbon cage. This bond structure corresponds to one of the stable candidates predicted by molecular orbital calculation, which accounts for the charge transfer interaction in $Y^{3+}C82^{3-}$ as has already been confirmed by ESR measurements.

Metallofullerenes have been produced by laser evaporation and arc-burning methods.[1] Mass spectrometry indicated the existence of a series of metallofullerenes, e.g., LaC82, YC82 and ScC82 and multiple-metal compounds such as Y2C82 and Sc2C82. Electron spin resonance (ESR) studies indicated the +3 oxidation state for the La and Y of the LaC82 and YC82 species.[2-4] Kikuchi et al.[5] and Shinohara et al.[6] have recently succeeded in purifying and isolating of metallofullerenes such as LaC82 and Sc2C82, respectively. Optical absorption spectra[5] and ultraviolet photoelectron spectra (UPS)[7] of the purified LaC82 strongly suggest that the metal atom is inside the cage. However, microscopic structure of metallofullerene is not sufficiently understood, because productivity in metallofullerenes is still very low. Extended X-ray absorption fine structures (EXAFS) are well known as powerful probes for studying the local atomic arrangement around the atom of a specific element, even if the amount of the sample is quite small. The first EXAFS study of YC82 has recently been reported by Sodeholm et al.[8] They proposed a dimer model like C82-Y-O-Y-C82 from the Y-Y interaction. More recently, Park et al.[9] have also conducted EXAFS measurements on the mixed sample of YC82 and Y2C82. However, the local structure around the Y atom in the YC82 compound is still not clear, since both Sodeholm and Park have dealt with sample containing almost the same amount of YC82 and Y2C82. Here, we proposed a Y-C

---

* Present Address: Joint Research Center for Atom Technology (JRCAT)
c/o National Institute for Advanced Interdisciplinary Research 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

bond structure in YC82 metallofullerene based on our EXAFS measurement of a sample containing only YC82 as the metallofullerene.

The YC82 compounds were produced by conventional contact-arc vaporization. A mixture of Y2O3, graphite, and phenol resin powder (weight ratio of 1:6:2) was pressed into columnar rods about 5 mm in diameter. The rods were then baked at 1100 °C for 5 h in a vacuum and evaporated into soot in a He atmosphere of about 300 torr. The final product was extracted with a benzene solution of the soot. The mass spectrum was measured using an FTMS-2000 (Extrel) in a negative-ion mode. Figure 1 shows a laser desorption-Fourier transform mass spectrum of the final product. Only the peak corresponding to YC82 can be clearly identified as metallofullerenes, at a mass number m/z=1073. Thus, YC82 is confirmed to be a major metallofullerene.

The EXAFS experiment was performed at beam line 7C of the Photon Factory, the National Laboratory for High Energy Physics. The spectrum was measured on the K-edge of Y in a transmission mode for the standard Y2O3, and in a fluorescence mode for the YC82, at room temperature. Synchrotron radiation was monochromatized with a Si(111) double-crystal monochrometer. Figure 2 shows the absorption spectrum u(hν) for YC82. The local atomic arrangement is obtained as the radial distribution through a Fourier transform of normalized EXAFS spectrum X(k), defined by $\{u(k)-u_0(k)\}/u_0(k)$, into r-space, where k is the wave number of emitted photoelectrons. The absorption-edge energy of Y was determined to be the steepest point of the edge energy curve, i.e., 17042 eV for Y2O3 and YC82. Since X(k) is the absorption coefficient per absorbed atom, we are able to determine the average bond structure in a YC82 molecule.

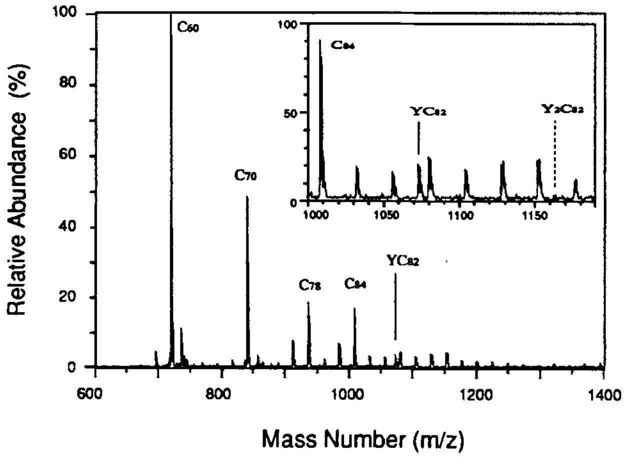

FIGURE 1 Negative-ion laser desorption-Fourier transform mass spectrum of benzene extracts containing YC82 metallofullerene. The inset shows the YC82 region on a magnified scale.

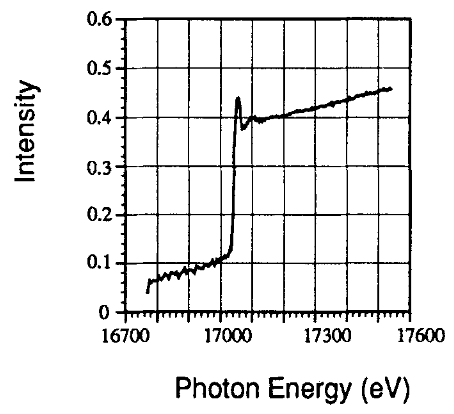

FIGURE 2 Yttrium K-edge X-ray absorption spectrum for YC82.

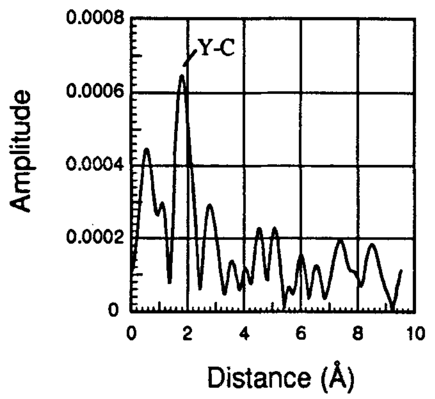

FIGURE 3 The Fourier transform of the normalized EXAFS data on YC82.

Figure 3 shows the radial distribution function obtained by Fourier transform of $k^2X(k)$ for YC82. The main peak at about 1.70Å was Fourier transformed into k-space so as to identify the elements of the neighboring atom. EXAFS oscillations (k=4-9Å^{-1}) caused by the neighboring atoms are denoted by the dotted-line in Fig. 4(a). From the envelope carbon, atoms are found to be bonded to the Y atom. The structual parameters of Y-C bonds, i.e., the Y-C bond length R(Y-C), coordination number N(C), and Debye parameter σ^2, were then determined by a curve fit analysis based on the spherical wave approximation of emitted photoelectrons.[10-12] The physical quantities required for calculation were obtained as follows. Phase shifts of the photoelectrons in the absorbing Y atom were taken from the numerical tables given by Teo and Lee.[13] Phase shifts for the scattering C and O atoms (ℓ=0-10) were calculated according to a program developed by Pendry[14] involving with core-state averaged function.[13] The amplitude reduction due to inelastic photoelectron scattering was evaluated in the form of $\exp(-2r/\lambda)$, where r is the interatomic path length and λ is the escape depth dependence on photoelectron energy.

The best fit for YC82 was achieved when the R(Y-C) was 2.41Å , N(C) was 0.95 and σ^2 was $(0.039)^2$Å^2, as shown by the solid line in Fig. 4(a). The R-factor of the fit is 0.23. It should be noted here that the experimental amplitude is dumped by shake-up and shake-down effects which, in turn, affects N(C) and σ^2. The results for standard Y2O3 should be used to correct the theoretical amplitude. The dumping factor can be estimated by adjusting the best-fitted oxygen coordination number, N(O), for Y2O3 to match the actual N(O). As shown in Fig. 4(b), the best fit for Y2O3 was achieved with

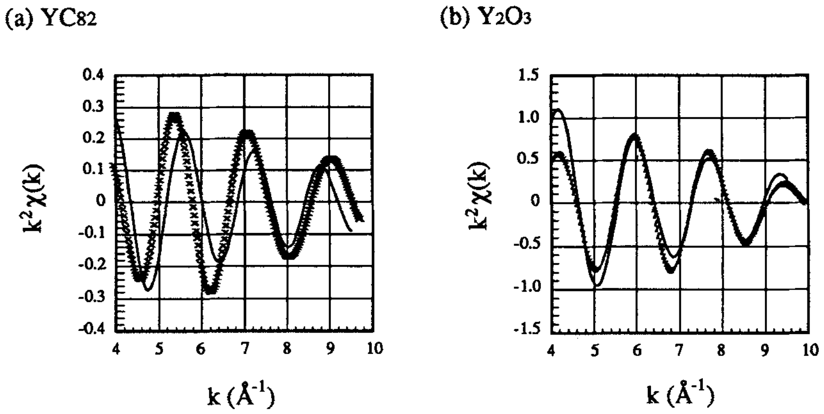

FIGURE 4. Back-transforms (dotted lines) of (a) Y-C peak for YC82 and (b) Y-O peak for Y2O3, and the respective best fits (solid line).

an R-factor of 0.18 when R(Y-O) was 2.31Å, N(O) was 2.9, and σ^2 was $(0.048)^2$Å^2. In Y2O3, a Y atom is surrounded by 6 nearest neighboring oxygen atoms. Thus, the N(C) of YC82 can be corrected by multiplying 0.95 by the factor of 6.0/2.9, yielding N(C)=1.9.

The significance of our results is the fact that two carbon atoms on average are coordinating a single Y atom. The following Y-arrangements two possibilities can be excluded: First, the Y atom is not on the vertical center line of the carbon rings since the coordination number would be 5 or 6 in this case. Second, the Y atom is not incorporated into the carbon network since the coordination number in this case would be 3. The structural model of the Y-C bond in YC82 is shown in Fig. 5(a). A Y atom and two carbons form an isosceles triangle. The Y atom is located on the double bond between two fused six-membered rings or between a five- and a six-membered ring in C82 with a distance of about 2.31Å. This local-bond structure resembles that of a typical charge transfer complex such as Ag^+·C6H6 [15] in coordination number 2. Thus, the Y atom is strongly attracted to π-bonding carbons due to the charge transfer interaction in the form of $Y^{3+}C82^{3-}$ as indicated by ESR measurements.[3,4] Furthermore, molecular orbital calculation reported that a La atom coordinating a carbon double bond between fused six-membered rings is energetically stable in $La^{3+}C82^{3-}$, retaining the C2 symmetry,[16] as shown in Fig. 5(b). However, it is not clear whether the C2 symmetry is the most stable and abundant. This configuration is about 7 kcal/mol more stable than that in which it is in the center of the cage, and indicates it has the charge transfer form of $La^{3+}C82^{3-}$. This energy gain related to the stabilization is lower than that for coordinating the center of a hexagonal ring. Accordingly, it is strongly supported that C82 forms a charge transfer complex with a metal atom through one of the double bonds in the cage.

This argument is not consistent with the results of Soderholm, et al.[8] Based on their results that a Y atom has 7±1 neighboring carbons at 2.35 Å and that it also has a neighboring Y at a distance of between 3 and 4 Å, they proposed a structure in which the two Y ions are each associated with different carbon cages in the dimer formation of C82-Y-X-Y-C82, where -X- is a bridging carbon or oxygen species. No X-Y-C82-fragment has been detected in their mass spectrum, although the X-Y-C82 fragment should be easily detected as well as the PrC82O detected by Ishibashi et al.[17] if it contains X-Y-C82. Consequently, circumstantial evidence goes against their dimer model. Moreover, since the mass spectrum in Ref. 8 shows a Y2C82 contribution, it is straightforward to assume that the Y-Y scattering is attributable to the Y-Y bonds of Y2C82 and/or residual Y2O3 in their sample. If so, the R(Y-C) and N(C) in Ref. 8 can be understood as the mixing of Y2O3, Y2C82 , and YC82 .

Park et al. have also conducted EXAFS experiments using sample containing mixed fullerenes, the YC82 and Y2C82 species.[9] Instead of directly analyzing the EXAFS data with duplicate neighboring shells, they showed that it could be explained plausibly with two coordinating shells: R(Y-C)=2.40Å, N(C)=6±1, $\sigma^2=(0.10)^2Å^2$ for the first shell; R(Y-C)=2.85Å, N(C)=6±1, $\sigma^2=(0.13)^2Å^2$ for the second shell. However, no unique structure for YC82 and Y2C82 can be derived from this data. The experiment should be conducted independently using highly purified YC82 and Y2C82 samples so as to avoid ambiguities.

We also performed EXAFS measurement on the L-III edge of the La in LaC82

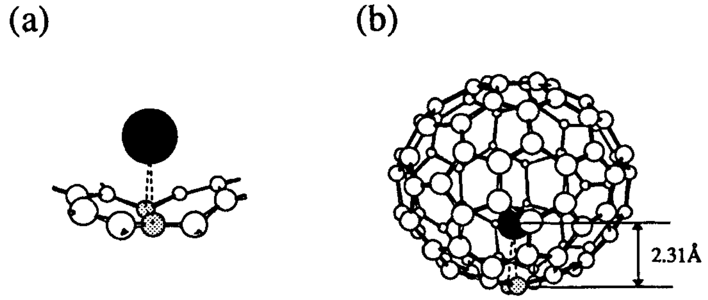

FIGURE 5 Schematic illustration of the bond structure of a Y atom in the YC82 metallofullerene. (a) The local bond structure in which a Y ion is located on the double bond between fused six-membered rings. (b) The structural model of endohedral metallofullerene YC82 retaining C2 symmetry. Solid and open circles indicate Y and C atoms.

prepared by the procedure described above. LaC_{82} was confirmed by mass spectrometry to be a major metallofullerene complex. The analysis showed that a La atom is bonded to nearly two carbons in LaC_{82} as well as in YC_{82}. Detailed analyses of these YC_{82} and LaC_{82} compounds are currently still in progress. Considering the results for the YC_{82} and LaC_{82}, it is suggested that metal positioning on a double bond due to a charge transfer interaction might be a general feature of metallofullerene systems.

ACKNOWLEDGMENTS

The authors are grateful to Y. Kikuchi of Sakuragawa Works, Hitachi Chemical Co., Ltd., for preparing the carbon-metaloxide rods. They also wish to express their sincere gratitude to H. Nakagawa and K. Aoyama of Newly Instruments Inc. for measuring the mass spectrum.

REFERENCES

1. Y. Chai, T. Guo, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, and R.E. Smalley, J. Phys. Chem., 95, 7564 (1991).
2. R.D. Johnson, M.S. de Vries, J. Salem, D.S. Bethune, and C.S. Yannoni, Nature, 355, 239 (1992).
3. J.H. Weaver, Y. Chai, G.H. Kroll, C. Jin, T.R. Ohno, R.E. Haufler, T. Guo, J.M. Alford, J. Conceicao, L.P.F. Chibante, A. Jain, G. Palmer, and R.E. Smalley, Chem. Phys. Lett.. 190, 460 (1992).
4. H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi, and Y. Ando, J. Phys. Chem., 96, 3571 (1992).
5. K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, and Y. Achiba, Chem. Phys. Lett.. 216, 67 (1993).
6. S. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, and Y. Saito, J. Phys. Chem., 97, 4259 (1993).
7. S. Hino, H. Takahashi, K. Iwasaki, K. Matsumoto, T. Miyazaki, S. Hasegawa, K. Kikuchi, and Y. Achiba, Phys. Rev. Lett., 71, 4261 (1993).
8. L. Soderholm, P. Wurtz, K.R. Lykke, D.H. Parker, and F.W. Lytle, J. Phys. Chem., 96, 7153 (1992).
9. C.H. Park, B.O. Wells, J. DiCarlo, Z.X. Shen, J.R. Salem, D.S. Bethune, C.S. Yannoni, R.D. Johnson, M.S. de Vries, C. Booth, F. Bridges, and P. Pianetta, Chem. Phys. Lett., 213, 196 (1993).
10. H. Kajiyama, A. Fukuhara, Y. Nishino, and S. Muramatsu, Phys. Rev. B, 38, 1938 (1988).
11. A.G. Mckale, B.W. Veal, A.P. Paulikas, S.K. Chen, and G.S. Knapp, J. Am. Chem. Soc., 110, 3763 (1988).
12. J. E. Muller and W. L. Schaich, Phys. Rev. B, 27, 6489 (1983).
13. B.K. Teo and P.A. Lee, J. Am. Chem. Soc., 101, 2815 (1979).
14. J.B. Pendry, J. Phys. C, 4, 2501 (1971): ibid. C, 5, 2567 (1972).
15. R.E. Rundle and J.H. Goring, J. Am. Chem. Soc., 72, 5337 (1950).
16. S. Nagase, K. Kobayashi, T. Kato, and Y. Achiba, Chem. Phys. Lett., 201, 475 (1993).
17. M. Ishibashi, Y. Tomioka, and Y. Taniguchi, Jpn. J. Appl. Phys., 33(2B), L258 (1994).