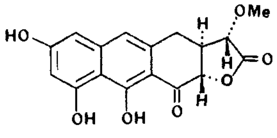
had been assigned by NMR studies of degradation product **24**



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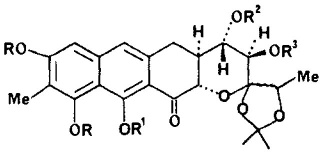

25: R = R³ = Ac; R¹ = H; R² = Me
26: R = R¹ = Me; R² = COC_6H_5; R³ = H

for olivin[12] and studies of cyclic bisketal **25**, a derivative of a potassium carbonate catalyzed rearrangement product of chromomycinone.[13] The absolute configuration at C-1′ in olivin was based on a CD comparison with D-*O*-methyl mandelic ester; while in chromomycinone, a benzoate **26** obtained from **25** was subject to an early interpretation of Davydov splitting in the CD (exciton chirality rule).[14] Hence, we believe that our synthesis using a known sugar and stereoselective chemistry confirms the assignments of relative and absolute configuration of olivin **3**.[15]

Acknowledgment. We are indebted to the National Cancer Institute for Grant CA 37359, which supported the work. The JEOL GX 400 NMR spectrometer used in this work was purchased with funds awarded by NSF-PCM 111745. We are grateful to Professor S. M. Weinreb for several helpful discussions, for making available unpublished experimental details of his work, for supplying comparison spectra, and for a gift of olivomycin A for use in the degradation to obtain authentic trimethylolivin.

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(12) Bakhaeva, G. P.; Berlin, Y. A.; Chuprunova, O. A.; Kolosov, M. N.; Peck, G. Y.; Piotrovich, L. A.; Schemyakin, M. M.; Vasina, I. V. *J. Chem. Soc., Chem. Commun.* **1967**, 10.

(13) Miyamoto, M.; Morita, K.; Kawamatsu, Y.; Kawashima, K.; Nakanishi, K. *Tetrahedron* **1967**, *23*, 411.

(14) Harada, N.; Nakanishi, K.; Tatsuoka, S. *J. Am. Chem. Soc.* **1969**, *91*, 5896.

(15) The structure assigned to each new compound was in accord with its infrared and 400-MHz ^1H NMR spectra. The key intermediates **9**, **13** (derivatized as its trimethylsilyl ether), and **16** were also analyzed by their high-resolution mass spectra.

$C_{60}La$: A Deflated Soccer Ball?

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A recent paper by Heath et al.[1] (HOZLCKTS) reported very exciting results; the production and detection of C_nLa complexes, n = 44, 46, 48, ...76, with n = 60 the dominant species. For the dominant C_nLa species, $C_{60}La$, the metal atom was postulated, on the basis of the experimental photoionization mass spectroscopy data, to be strongly bound within a spheroidal carbon shell possessing unusually high stability. In this paper we present further experimental evidence which when added to the information presented by HOLCKTS and Kroto et al.[2] (KHOCS) seriously challenges this enticing conclusion.

Three experimental observations compelled HOZLCKTS to confidently propose this novel structure. First, KHOCS reported that C_{60} was the most intense bare cluster ion observed in the photoionization mass spectra (PMS) of bare carbon clusters; second, when a lanthanum-impregnated graphite substrate was vaporized, $C_{60}La$ was the most intense C_nLa lanthanum-containing cluster ion; third, only C_nLa complexes containing one lanthanum atom were detected in the PMS.

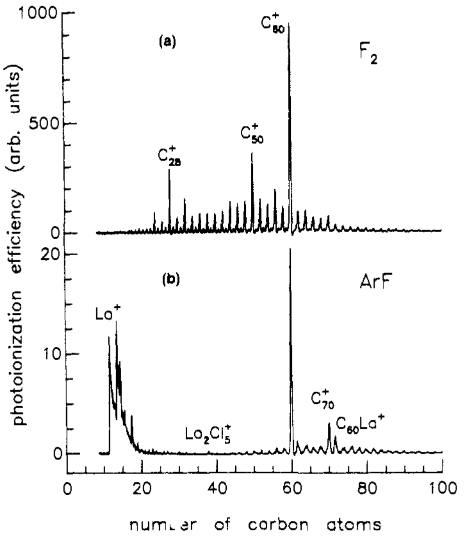

Figure 1. Photoionization time of flight mass spectra obtained from pulsed-laser vaporization of a lanthanum-impregnated graphite rod is shown for (a) ionization by F_2 and (b) ionization by ArF. The lower panel (b) was obtained when unfocused ArF (6.42-eV photons, 1.17 mJ/pulse) was the ionizing laser while the upper panel (a) was obtained when unfocused F_2 (7.87-eV photons, 0.05 mJ/pulse) was the ionizing laser. Except for the fact that the multiplier gain was reduced a factor of 2.6 for (a), all other experimental parameters were identical. The ionizing laser beam was collimated by a 0.125 cm high by 1.0 cm long slit. the vaporization laser intensity was ~360 MW/cm² (28 mJ at 532 nm of which ~50% was focused to a 1-mm-diameter spot on the lanthanum-impregnated graphite rod). The cluster source geometry simply consisted of the pulsed nozz' operated with 10 atm of helium backing pressure. The helium pulse ses through a 0.1-cm-diameter tube. At the graphite rod located 0. m from the nozzle exit, this tube opens up to 0.2-cm diameter for a gth of 4.5 cm before exiting to vacuum.

In addition to confirming the above experimental observations, we have found that (a) all[3] C_nLa^+ have ionization thresholds below 6.42 eV, the ArF photon energy, whereas, under identical conditions, bare C_n, n = 40–100, have ionization thresholds above 6.42 eV,[4] (b) all C_n and C_nLa clusters for n = 44–76 have ionization thresholds below 7.87 eV, the F_2 photon energy, and (c) the photoionization efficiency (ions produced per unit photon flux) for C_n^+ is 2 orders of magnitude larger when ionizing with 7.87-eV photons than it is with 6.42-eV photons, whereas it is only a factor of 2–4 larger for C_nLa^+. Such effects significantly alter the magnitude of the C_n^+ signals relative to the C_nLa^+ signals and, if not taken into account, can lead to erroneous conclusions regarding the relative abundance of the corresponding neutral parent species.

The lower trace in Figure 1 shows the time of flight mass spectrum obtained for ionization with 6.42 eV (ArF). For the clusters containing 40–80 atoms, Figure 1b is in all respects quite similar to that published by HOZLCKTS. The most intense peaks are C_{60}^+, C_{70}^+, and $C_{60}La^+$. The weaker peaks are $C_{n-12}La^+$, 5 amu to the low-mass side of C_n^+. The upper trace was obtained under identical operating conditions except that the ionization was with 7.87-eV photons with substantially less photon flux (see figure caption for details). The major difference between Figure 1, parts a and b, in the 40–80 cluster size range is that in Figure 1b the peaks (except for C_{60}^+ and C_{70}^+) are C_nLa^+, whereas in Figure

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(1) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779–7780.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162–163.

(3) Only results for even atom clusters are discussed here.

(4) Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A., unpublished results. This paper will detail our results for bare C_n clusters. We find that the large variations the C_{60} ion signal can be understood as an interplay between large chang in photoionization efficiency and fragmentation pathways dependent upon ionizing laser frequency and intensity. The C_{60}^+ signal exhibits a complex dependent on ArF ionizing laser intensity, which depends upon the specific experimental conditions. It exhibits either a linear or a quadratic dependence on the ArF ionizing laser intensity dependent upon the *ionizing* laser intensity, the *vaporizing* laser intensity, and/or the *length* of a 2-mm diameter extender tube through which the evaporated material must pass.

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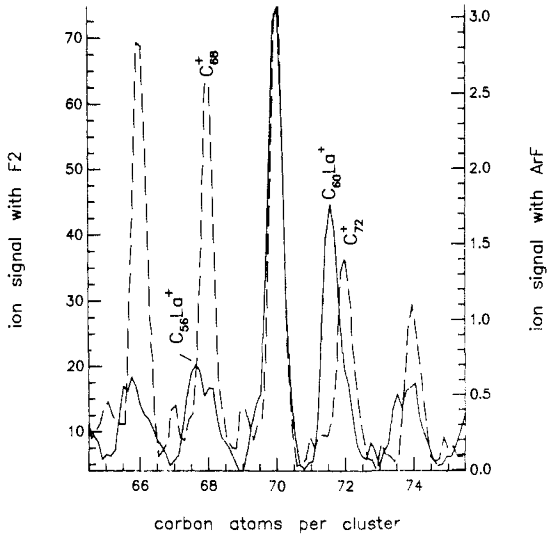

Figure 2. Expanded view of Figure 1 for the mass region spanning clusters containing 66–74 carbon atoms. The solid line and right-hand ordinate refer to the spectrum taken with ArF ionization and the dashed line and left-hand ordinate refer to the spectrum taken with F_2 ionization.

1a all the peaks are bare C_n. The C_nLa^+ ions are still present in Figure 1a but only appear as weak shoulders on the low-mass side of the bare cluster ions. This is more readily evident in Figure 2, which compares an expanded section of the two spectra presented in Figure 1. For quantitative comparison, these spectra are normalized to photon flux, which is reflected in the ordinate values. For these spectra we find that the photoionization efficiency for producing $C_{60}La^+$ is only 2–4 times larger with 7.87 eV than it is with 6.42 eV. On the other hand, the photoionization efficiency for producing the bare cluster ions, e.g., C_{60}^+, shows a dramatic increase of a factor of 50–100 with 7.87 eV compared to that with 6.42 eV.

Such dramatic changes in ion yields are due to the differing photophysical processes producing C_nLa^+ and C_n^+ during the ionization process. Both C_nLa^+ and C_n^+ ion signals vary linearly with F_2 ionizing laser intensity[5] at low intensity. Thus the spectrum obtained with F_2 should more closely approximate the actual neutral cluster concentration in the beam. With ionization at 7.87 eV the $C_{60}La^+$ signal is only 1–2% of the C_{60}^+ signal. If the $C_{60}La_2^+$ signal is also only 1–2% of the $C_{60}La^+$ as is reasonable in a sequential reaction, then observation of no signal on $C_{60}La_2^+$ for either ArF or F_2 ionization is *not* unexpected. $C_{60}La_2^+$ is simply produced in so small abundance as to be undetectable.[7] This together with the observation of a large number of C_nLa complexes may be more suggestive that the La atom is attached to the edge or face of graphite flakes rather than residing at the center of a spheroidal shell as proposed by HOLCKTS.

Finally, with ArF ionization a large "blob" of low-mass fragment ions is produced. The sharp peaks are assigned to La^+, LaC_2^+, $LaCl^+$, $LaCl_2^+$, LaC_4^+, $La_2Cl_5^+$, etc. The peak signal for these ions occurs *later* in time than the peak signal for the heavier mass C_nLa^+ which strongly suggests that they are fragments from very large clusters, C_nLa, $n \gg 60$. The total ion signal in this low-mass region is considerably larger than the C_{60}^+ or $C_{60}La^+$ signals when the ion signals are summed over all arrival times and corrected for transmission efficiency. These low-mass ions are produced when ionizing with ArF (0.4–1.8 mJ/pulse) or KrF[8] (5.0 eV, 1-2 mJ/pulse) but are absent when F_2 ($\leq$0.05 mJ/pulse) is the ionizing laser. Since the free La atom has an IP of 5.61 eV, it should be single-photon ionized by either 6.42- or 7.87-eV photons. Its appearance, as well as the appearance of all the low-mass ions containing La, in the 6.42-eV PMS but absence in the F_2 one strongly supports the contention that (a) substantial fragmentation is being induced by the higher intensity ArF[4] and (b) the lanthanum is complexed to carbon clusters.

In conclusion we show that under a specific set of experimental conditions certain ions may appear incredibly intense, whereas under a slightly different set of conditions these same ions may appear only weakly and/or other ions become quite intense.[9] Attempting to infer structural or stability information about neutral clusters simply from an intense (or weak) ion signal in a PMS is frought with complications which can lead one astray. However, the search for ultrastable structures, such as $C_{60}La$, i.e., a reinflated soccer ball, should not be abandoned, but rather a high priority should be put on developing techniques to perform direct structural characterization of such species.

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(5) In our earlier work[6] we found that carbon clusters containing 40–80 atoms exhibited a linear dependence on ArF and KrF ionizing laser intensity. At that time we interpreted such behavior to mean that the ionization threshold for direct ionization was lower than 6.42 and 5 eV. Under the experimental conditions of those experiments (short extender length 1.27 cm and high vaporizing laser intensity 300–400 MW/cm^2), we were most likely dealing with internally hot clusters[9] undergoing substantial fragmentation during the ionization process.

(6) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322-3330.

(7) When potassium-containing graphite rods are vaporized, clusters of the form C_nK, C_nK_2, and C_nK_3 are easily observed in the PMS.

(8) With ionization by KrF the C_n^+, and C_{60}^+, in particular, are quite weak compared to ArF whereas the signal level of the low-mass "blob" is nearly the same.

(9) We have observed similar behavior in our studies of silicon clusters, also molecular clusters. Trevor, D. J.; Cox, D. M.; Reichmann, K. C.; Kaldor, A., submitted for publication in *J. Chem. Phys.*

Electrochemical Preparation of Triplatinum Complex with a Linear Structure and Its Transformation to an A-Frame Structure

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The complexes containing metal–metal bonds have been the subject of reactivity and physical characterization. A-frame complexes have also been increasing attention on systematic cooperative binding and activation of substrates.[1] Recently Hoffman and Hoffmann employed the isolobal analogy between CH_2 d^{10} ML_2 and d^8 ML_4 metal fragments to predict the existence of a trimetallic cluster with one long and two short M–M bonds, a so-called "A-frame" with bridging ML_2 moiety.[2] To date, no complexes have been obtained.

Here we report a new aspect of the chemistry that led to the preparation and structure of linear and A-frame triplatinum complexes. The potentiostatic electrolysis of $[Pt(2,6\text{-}Me_2C_6H_3NC)_4](PF_6)_2$ (**1**) in CH_3CN containing 0.1 M $NaClO_4$ was carried out by means of a mercury pool electrode at −1.40 V.[3] The electrolysis consumed ca. 1.5 F and gave pale yellow and yellow crystals, formulated as $[Pt_2(2,6\text{-}Me_2C_6H_3NC)_6](PF_6)_2 \cdot CH_2Cl_2$ (**2**) (14%)[4] and $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_8](PF_6)_2$ (**3**) (47%),[5] respectively. Complex **2** was assigned as a dimer by its

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(1) Balch, A. L. *Homogeneous Catalysis with Metal Phosphine Complex*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 167. Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(2) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

(3) The potentials are indicated against a saturated calomel electrode (SCE), although a $Ag/AgNO_3$-TBAP-CH_3CN electrode was employed.

(4) Anal. Calcd for $C_{55}H_{56}N_6P_2F_{12}Cl_2Pt_2$: C, 42.56; H, 3.64; N, 5.41. Found: C, 42.87; H, 3.61; N, 5.44. ^1H NMR (CD_2Cl_2): δ 2.56 (2,6-Me), 5.31 (CH_2Cl_2), ca. 7.2 (Ar H).

(5) ^1H NMR (CD_2Cl_2): δ 2.27 (2, 2,6-Me), 2.47 (1, 2,6-Me), ca. 7.2 (Ar H). Anal. Calcd for $C_{72}H_{72}N_8P_2F_{12}Pt_3$: C, 44.93; H, 3.77, N, 5.82. Found: C, 45.42, H, 3.81; N, 5.93.

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