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M.R. Smith III, P.T. Matsunaga, and R.A. Andersen

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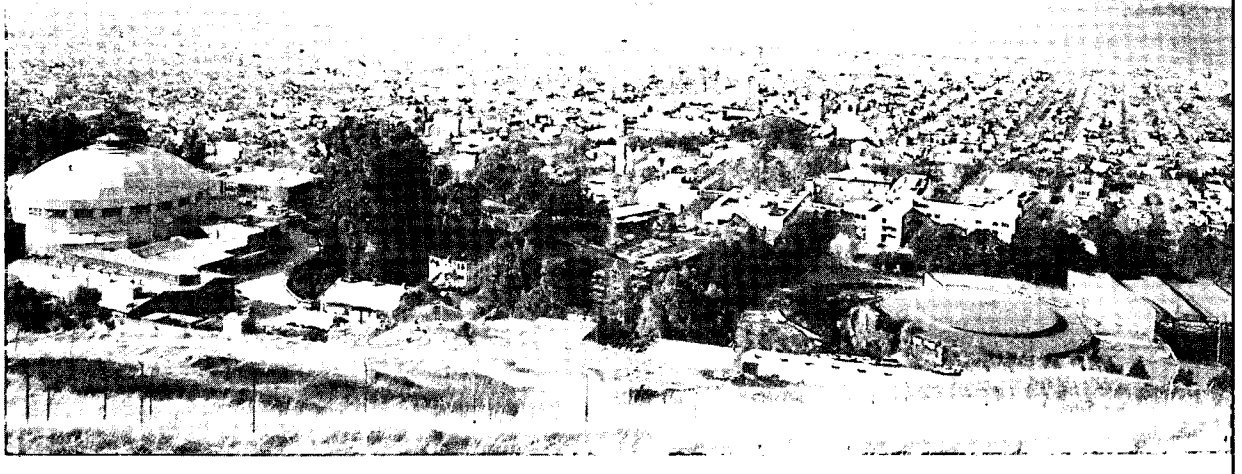

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Preparation of Monomeric $(Me_5C_5)_2VO$ and $(Me_5C_5)_2Ti(O)(L)$ and their Decomposition to $(Me_5C_5)_4M_4(\mu\text{-}O)_6$

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Abstract

The vanadium metallocene, $(Me_5C_5)_2V$, reacts with N_2O (4 atm, room temperature) to give $(Me_5C_5)_2VO$ ($\nu VO = 855\ cm^{-1}$, $\nu V^{18}O = 820\ cm^{-1}$) as green-brown crystals from hexane. The vanadyl is monomeric in the gas phase (M^+ in the mass spectrum) and paramagnetic with $\mu_B = 1.95$ ($\theta = 0.49$ K from 5-300 K). An isotropic EPR spectrum is observed in methylcyclohexane at room temperature which consists of eight-lines with $g_{iso} = 1.9844$ and $A_{iso} = 25$ G. Similarly, reaction of $(Me_5C_5)_2Ti(C_2H_4)$ with N_2O in a mixture of pyridine-tetrahydrofuran yields monomeric, diamagnetic $(Me_5C_5)_2Ti(O)(py)$ as orange crystals ($\nu TiO = 852\ cm^{-1}$, $\nu Ti^{18}O = 818\ cm^{-1}$). The derivative, $(Me_5C_5)_2Ti(O)$(4-phenylpyridine), crystallizes as a toluene solvate in the triclinic space group $P\bar{1}$ with a = 10.407(2)Å, b = 12.998(4)Å, c = 13.2597(2)Å, α = 79.90(2)°, β = 67.42(1)°, γ = 83.02(2)°. The geometry about the titanium is pseudo-tetrahedral with Ti-O = 1.665(3)Å. Both oxo-metallocenes decompose (M = V at room temperature, M = Ti with gentle warming) to the known tetranuclear compounds $(Me_5C_5)_4M_4(\mu\text{-}O)_6$, M = V, Ti. Mass spectroscopic studies on the ^{18}O-labelled compounds show that all of the label in the tetranuclear compounds are derived from the monomeric precursors in a complex net reaction that results in the MO unit going to the M_4O_6 unit.

Nitrous oxide is a convenient source of oxygen atoms for the synthesis of oxo-metallocenes (and the products derived therefrom) as well as the insertion of oxygen into metal-hydrogen or -carbon bonds.[1,2] Reaction of nitrous oxide with either Cp_2Ti or Cp_2V gives $(Cp_2Ti)_2(\mu\text{-}O)$[3] or $Cp_5V_5(\mu\text{-}O)_6$,[4] respectively. On the other hand, the pentamethylcyclopentadienyl analogues give $(Me_5C_5)_2Ti_2(CH_2C_5Me_4)(\mu\text{-}O)_2$[5] or $(Me_5C_5)_4V_4(\mu\text{-}O)_6$,[6] respectively. Monomeric oxo-metallocenes, Cp_2MO or $(Me_5C_5)_2MO$ where M is Ti or V, were neither observed nor isolated, an observation we thought curious since $(RC_5H_4)_2MO$ (M = Mo or W)[7] and $(Me_5C_5)_2WO$[8] have been isolated and $(Me_5C_5)_2ZrO$ has been generated and trapped by reactions with acetylenes.[9] In this communication we show that $(Me_5C_5)_2VO$ and $(Me_5C_5)_2Ti(O)(L)$, where L is pyridine or a substituted pyridine, can be isolated in reactions between nitrous oxide and the metallocenes and that they decompose to the known tetranuclear materials, $(Me_5C_5)_4V_4(\mu\text{-}O)_6$[6] and $(Me_5C_5)_4Ti_4(\mu\text{-}O)_6$.[10]

Exposing a red hexane solution of $(Me_5C_5)_2V$ to nitrous oxide (4 atm.) yields a green-brown solution and a black precipitate. Green-brown crystals of $(Me_5C_5)_2VO$[11] may be isolated from the solution in 45% yield on cooling. The black precipitate was shown to be $(Me_5C_5)_4V_4(\mu\text{-}O)_6$ by infrared and mass spectroscopy.[6] Paramagnetic $(Me_5C_5)_2VO$ is a monomer in the mass spectrum, and the solid state IR shows $\nu V = O$ at 855 cm^{-1} which shifts to 820 cm^{-1} on isotopic substitution(^{18}O). In the solid state, the compound follows Curie behavior since a plot of χ_M^{-1} is a linear function of temperature (5-300 K) with μ_B = 1.95 B.M. and θ = -0.49 K. The EPR spectrum at room temperature in methylcyclohexane (ca. 0.1 M) consists of an eight-line pattern with g_{iso} = 1.9844 and A_{iso} = 25G. Both data are in the range expected for bent metallocenes with a $3d^1$ electron structure.[12]

Similarly, exposure of $(Me_5C_5)_2Ti$,[13a] or better $(Me_5C_5)_2Ti(C_2H_4)$,[13b] to N_2O (4 atm.) in pentane yields a green insoluble material whose ^1H NMR spectrum in C_6D_6 indicates a mixture of compounds; resonances for $(Me_5C_5)_2Ti(CH_2C_5Me_4)(\mu\text{-}O)_2$ and

$(Me_5C_5)_2Ti_4(\mu\text{-}O)_6$ can be identified. Since the hypothetical $(Me_5C_5)_2TiO$ has a vacant metal based orbital of a_1-symmetry (half-occupied in the case of $(Me_5C_5)_2VO$), we postulated that this vacancy was the source of instability of the monomeric species. If true, doing the reaction in presence of a two-electron donor should give $(Me_5C_5)_2Ti(O)(L)$. Addition of nitrous oxide (1 atm.) to a solution of $(Me_5C_5)_2Ti(C_2H_4)$ dissolved in a 1:10 solution of pyridine:tetrahydrofuran results in an instantaneous color change from green to orange and production of orange crystals of $(Me_5C_5)_2Ti(O)(py)$[14a] on cooling the solution to -80°C in 59% yield. The titanium compound is diamagnetic and $\nu Ti = O$ is observed at 852 cm^{-1} which shifts to 818 cm^{-1} in the O^{18}-labelled isotopomer. The mass spectrum shows a monomeric $[M\text{-}py]^+$ ion in the gas phase, see below. Using 4-phenylpyridine rather than pyridine gave orange crystals of $(Me_5C_5)_2Ti(O)$(4-phenylpyridine) upon crystallization from toluene that were suitable for an X-ray crystallographic study.[14b] An ORTEP diagram is shown in Figure I for the toluene solvate.[15] The geometry at the titanium center is similar to that found in $(Me_5C_5)_2TiCl_2$,[16] the principal difference being that the averaged Ti-C distances in the titanyl are longer (2.51 ± 0.05Å vs. 2.44 ± 0.02Å). The spread in the individual distances is wider, presumably reflecting greater steric congestion about the titanyl center. The Ti-O bond distance of 1.665(3)Å is in the range (1.61 to 1.68Å) found in six structures of titanyl groups with vastly different ligands.[17]

The decomposition of the monomeric oxo-metallocenes is not necessarily a simple event since four (M = O) units generate the M_4O_6 units with loss of four Me_5C_5 groups; the extra two oxygen atoms could arise from two additional M = O units as illustrated in eq. 1 and 2 or from advantitious water or oxygen, Cp_2^*MO being replaced by "O" in eq. 2.

$$4\ Cp_2^*MO \rightarrow (Cp^*MO)_4 + 4\ Cp^* \qquad (1)$$

$$2\ Cp_2^*MO + (Cp^*MO)_4 \rightarrow Cp_4^*M_4O_6 + 2\ Cp_2^*M \qquad (2)$$

In order to address this question we isolated the ^{18}O-labelled compounds $(Me_5C_5)_2V(^{18}O)$ or $(Me_5C_5)_2Ti(^{18}O)(py)$ and allowed them to decompose to $(Me_5C_5)_4V_4(^{18}O)_x(^{16}O)_{6-x}$ at room temperature or $(Me_5C_5)_4Ti_4(^{18}O)_x(^{16}O)_{6-x}$ at higher temperature. The tetranuclear compounds were analyzed by electron-ionization mass spectroscopy as the unlabelled compounds yield molecular ions. Figure IIa shows the mass spectrum of unlabelled $(Me_5C_5)_4Ti_4(O)_6$. The bar graphs represent the experimental intensities (shaded) and the calculated intensities (unshaded). Inspection shows that the calculated spectrum matches the experimental spectrum closely. The mass spectrum of $(Me_5C_5)_2Ti(^{18}O)(^{16}O)(py)$ shows a molecular ion for $[(Me_5C_5)_2Ti(^{18}O)(^{16}O)]^+$ from which the isotopic ratio of ^{18}O:^{16}O was determined to be 0.60:0.40. The decomposition of this mixed isotopomer gives the tetranuclear species whose experimental and calculated mass spectra are illustrated in Figure IIb. The calculated spectrum was derived by assuming that all of the oxygen atoms are exclusively derived from the monomer of isotopic composition ^{18}O:^{16}O = 0.60:0.40, rather than from some other source of ^{16}O atoms.[18] Inspection shows that, under this assumption, the experimental and calculated mass spectra match very well. This is consistent with, but does not prove, our assumption that the assembly of the $(Me_5C_5)_4Ti_4(O)_6$ occurs predominantly from $(Me_5C_5)_2TiO$. A similar conclusion can be reached for the decomposition of $(Me_5C_5)_2V(^{18}O_{0.76})(^{16}O_{0.24})$ to $(Me_5C_5)_4V_4[(^{18}O_{0.76})(^{16}O_{0.24})]_6$.[18] We conclude that the prolonged incubation times used by Bottomley[6] precludes isolation of monomeric $(Me_5C_5)_2VO$ and that the titanyl analogue can be stabilized by use of a two-electron, sigma-donor Lewis base.

Acknowledgment. We thank the Miller Institute for a post-doctoral fellowship (MRS), Ms. Sheri Ogden for her help with the mass spectra, and Dr. F.J. Hollan der for his help with X-ray crystal structure. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Supplementary Material Available. Tables of positional parameters, thermal parameters, bond lengths and bond angles, and crystal data (13 pages). Details for the mass spectral simulation of the molecular ions derived from $(Me_5C_5)_4V_4(^{18}O:^{16}O)_6$ and $(Me_5C_5)_4Ti_4(^{18}O:^{16}O)_6$ (5 pages). Ordering information is given on any current masthead page.

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11. Anal. Calcd $C_{20}H_{30}OV$: C, 71.2; H, 8.96. Found: C, 71.3; H, 8.99. EIMS: 337 (obs I = 100, calc I = 100) and 338 (25,22).

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14. (a) Anal. Calcd for $C_{25}H_{35}NOTi$: C, 72.6; H, 8.53, N, 3.13. Found: C, 72.6; H, 8.56; N, 3.08. The EIMS gave a parent ion for $[M\text{-py}]^+$, 334 (100,100), 335 (38,29). ^1H NMR (C_6D_6, 20°C): δ 8.91 (1H), 7.50 (1H), 6.74 (1H), 6.44 (2H), 1.86 (30H). The first four resonances are due to coordinated pyridine since they change to those values found for free pyridine in C_6D_6 upon addition of excess pyridine-d_5. (b) ^1H NMR (C_6D_6, 20°C): δ 9.00 (1H), 7.58 (1H), 7.18 (2H), 7.10 (3H), 6.88 (2H), 1.93 (30H). All of the resonances are complicated multiplets except the last one, due to Me_5C_5 that is a singlet.

15. The compound crystallizes in the triclinic crystal system in space group $P\bar{1}$ with cell dimensions (-92°C) a = 10.407(2)Å, b = 12.998(4)Å, c = 13.257(2)Å, α= 79.90(2)°, β = 67.42(1)°, γ = 83.02(2)°, V = 1627.3Å^3 with Z = 2 and d(calc) = 1.19 gcm^{-3}. The data were collected on a Nonius CAD4 automated diffractometer with MoK$_\alpha$ X-rays (λ = 0.71073Å) at -92°C. The structure was solved from Patterson and electron density maps and refined by full matrix least squares to a conventional R factor of 0.0609 (Rw = 0.0790, R_{all} = 0.0811 and GOF = 2.28) by using 3561 absorption corrected (empirical) data where $F_o^2 > 3\sigma (F_o^2)$ against 371 variables, the number of reflections collected was 4665 (+h, ±k, ± ℓ). All non-hydrogen atoms were refined with anisotropic thermal parameters; some but not all of the hydrogen atoms were located in the difference Fourier map. All of the hydrogen positions were calculated, based upon an idealized geometry and assigned thermal parameters equal to 1.4Å^2 larger than the carbon atom to which they are bonded, and were included in structure factor calculations but were not refined by least squares. A secondary extinction coefficient was included and refined upon.

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18. The details of the calculation as well as the spectra for the vanadium compound are given in the Supplementary Materials.

Figure Captions

Figure I: ORTEP diagram of $(Me_5C_5)_2Ti(O)$(4-phenylpyridine) (Toluene), solvate toluene is not shown. Ti-C (ave.) = 2.51 ± 0.05Å (rms deviation), Ti-Cp (centroid) = 2.20Å, TiO = 1.665(3)Å, TiN = 2.215(4)Å, Cp (centroid)-Ti-Cp (centroid) = 135°, Cp (centroid)-Ti-O = 108°, Cp (centroid)-Ti-N = 103°, and O-Ti-N = 90.8(1)°.

Figure II: (a) The upper spectrum is for $(Me_5C_5)_4Ti_4(O)_6$; the vertical bars that are shaded are the experimental intensities and the unshaded bars are the calculated intensities. (b) The lower spectrum is for $(Me_5C_5)_4Ti_4$ $(^{18}O:^{16}O = 0.60:0.40)_6$.

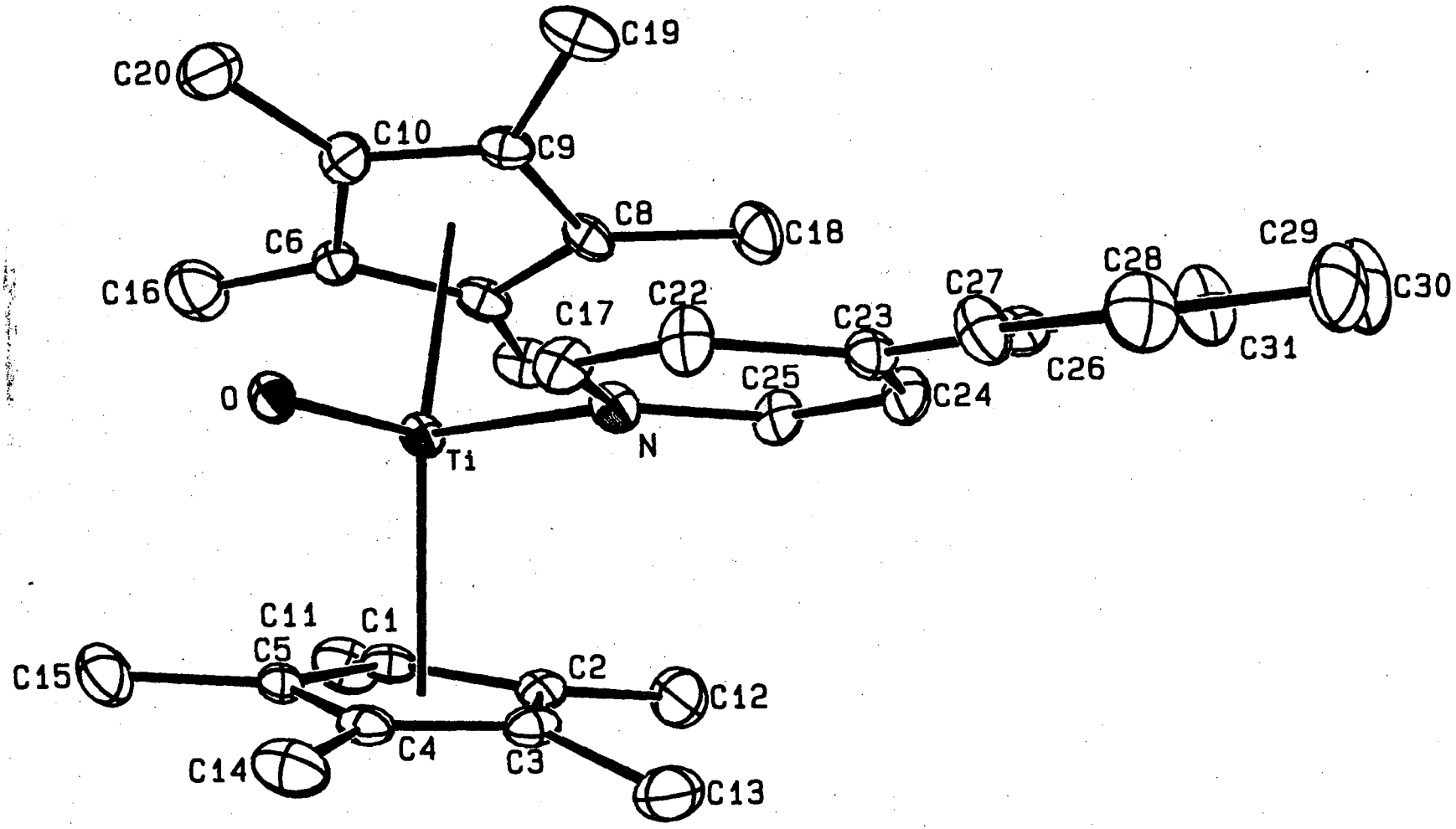
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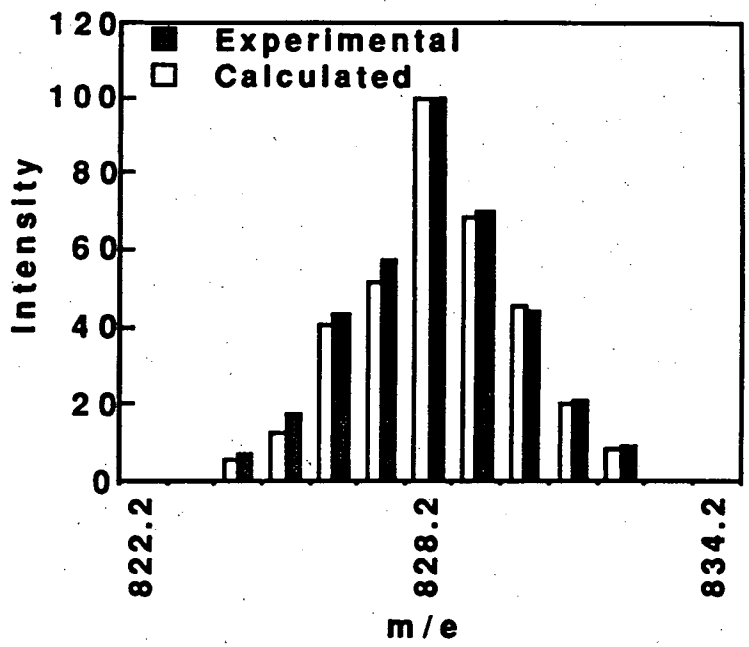
Figure I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20
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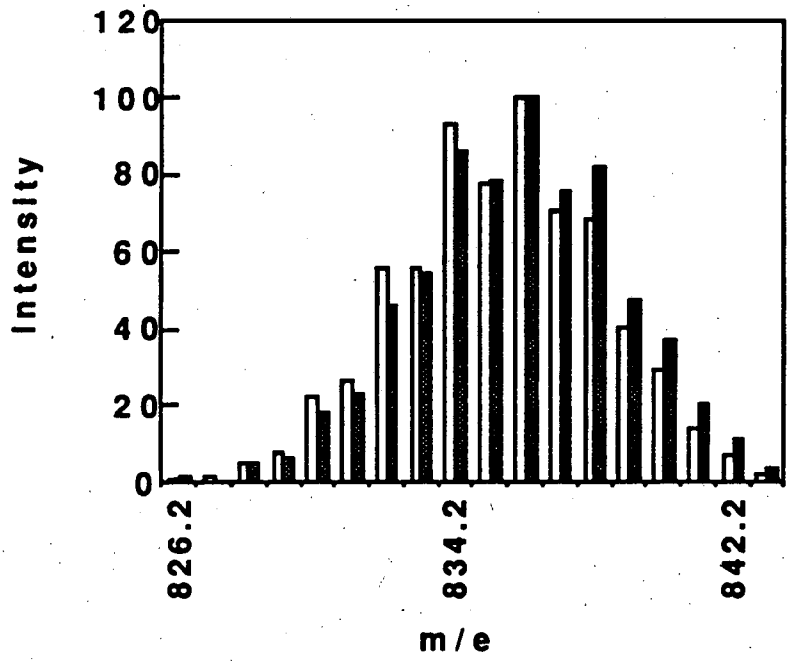
828.2
834.2
m/e

(a)


Intensity
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100
80
60
40
20
0
826.2
834.2
842.2
m/e

(b)

Figure II

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