

NMR(CDCl₃) δ 106; ¹H NMR (CDCl₃) δ 7.7 (broad 10 H), 6.7 (d, ²J_{PH} = 22 Hz, 1 H), 5.2 (s, 5 H), 2.4 (broad, 6 H); IR (Nujol) ν_{CO} = 2020, 1995 cm⁻¹. Anal. Calcd for C₂₁H₂₁IN₂O₂PFe: C, 55.2; H, 4.8; N, 6.1; Found: C, 54.8; H, 4.75; N, 5.7.

Crystallography. Crystals of **2** and the iodide salt of **3** were sealed under nitrogen in Lindeman glass capillaries and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Crystal and data collection parameters are listed in Table I. Structures were solved by using SHELXS⁸ and refined by using the SHELX system of computer programs.⁹

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Supplementary Material Available: For **2** and **3**, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (15 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

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Reaction between [(TPP)Ru(CO)]⁻ and Methyl Iodide. Evidence for Formation of a Ruthenium(II) Carbonyl Methylated Tetraphenylchlorin Derivative

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Introduction

The electroreduction of (P)Ru(CO), where P = the dianion of a given porphyrin ring, has been extensively investigated in nonaqueous media.¹⁻⁷ Two well-defined one-electron reductions are generally observed, and stable electroreduction products are obtained in virtually all nonaqueous solvents except for dichloromethane and dichloroethane, which rapidly react with the singly reduced species to give an overall irreversible electroreduction.^{2,3,6}

The first electroreduction of cobalt(II),⁸ nickel(II)⁹ and rhodium(III)^{10,11} porphyrins is also irreversible in CH₂Cl₂ and, in the

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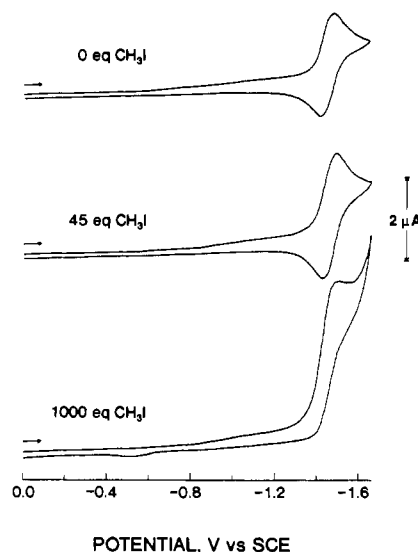


Figure 1. Cyclic voltammograms of 1.1×10^{-3} M (TPP)Ru(CO) in THF, containing 0.2 M TBAP and 0, 45, and 1000 equiv of CH₃I.

case of the cobalt and rhodium derivatives, is due to the formation of σ -bonded porphyrin complexes, as demonstrated by the isolation and characterization of (TPP)Co(CH₂Cl)⁸ and (TPP)Rh(CH₂Cl),¹⁰ where TPP = the dianion of tetraphenylporphyrin. The formation of a CH₂Cl adduct occurs via an oxidative addition reaction that is similar to those involving alkyl or aryl halides (RX) and [(TPP)Co]⁻ or [(TPP)Fe]⁻ to give free X⁻ and a σ -bonded porphyrin complex of the type (TPP)M(R).¹²

σ -Bonded (TPP)Ru(C₂H₅) and (TPP)Ru(C₂H₅)₂ complexes have also been synthesized from chemically reduced [(TPP)Ru]₂ and C₂H₅X,^{13,14} but a reaction between chemically or electrochemically reduced (P)Ru(CO) and alkyl halides has never been reported. This was investigated in the present study for electrogenerated [(TPP)Ru(CO)]⁻ and CH₃I. The resulting porphyrin product was not a σ -bonded methyl complex but rather was a methylated ruthenium(II) carbonyl chlorin. The formation of this species was monitored by in situ UV-visible and FTIR spectroelectrochemistry and the resulting final product identified by fast atom bombardment (FAB) mass spectrometry and electrochemistry.

Experimental Section

Instrumentation. Cyclic voltammetric measurements were obtained with an IBM EC 225 voltammetric analyzer. A platinum button served as the working electrode, and a platinum wire, as the counter electrode. A saturated calomel electrode (SCE) was separated from the bulk solution by a fritted-glass disk and was used as the reference electrode. Bulk controlled-potential coulometry was performed on an EG&G Princeton Applied Research Model 173 potentiostat which contained a Model 179 coulometer system that was coupled with a Princeton Applied Research Model RE0074 time base X-Y recorder. Thin-layer spectroelectrochemical measurements were made with an EG&G Princeton Applied Research Model 173 potentiostat coupled with a Tracor Northern 6500 rapid scan spectrometer. Construction of the thin-layer cell is described in the literature.¹⁵

Infrared measurements were carried out by using an IBM 32 FTIR spectrometer and an FTIR spectroelectrochemical cell whose construction and application have been described in the literature.^{2,16} Mass spectra were recorded on a VG-70 SEQ mass spectrometer and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Materials. Reagent grade tetrahydrofuran (THF) was distilled first from CaH₂ and then from Na-benzophenone. Dimethylformamide (DMF) and benzonitrile (PhCN) were vacuum distilled from activated

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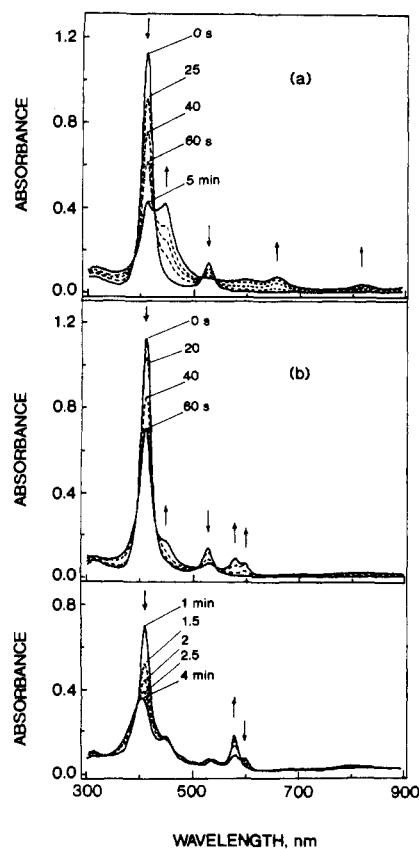


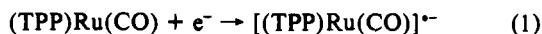
Figure 2. UV-visible spectral changes obtained during controlled-potential reduction of (TPP)Ru(CO) at -1.60 V (a) from 0 to 5 min in THF containing 0.2 M TBAP and (b) from 0 to 4 min in THF containing 0.2 M TBAP and 700 equiv CH_3I .

4-Å molecular sieves and P_2O_5 , respectively. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co., purified by two recrystallizations from ethyl alcohol, and stored in a vacuum oven at 40°C . Methyl iodide was purchased from Aldrich Chemical Co. and used without further purification. (TPP)Ru(CO) was synthesized according to the procedure of Rillema et al.⁶

Results

Electrochemistry and Spectroelectrochemistry. (TPP)Ru(CO) in THF undergoes a reversible room-temperature one-electron reduction at $E_{1/2} = -1.46$ V.^{2,3} This reduction remains reversible in THF containing up to 400 equiv of CH_3I but becomes irreversible in solutions with higher CH_3I concentrations. There is also an increase in the maximum cathodic peak current, and this is illustrated in Figure 1 by cyclic voltammograms obtained in THF containing 0, 45, and 1000 equiv of CH_3I . Under the latter solution conditions, the reduction is totally irreversible in that no reoxidation peak is coupled to the initial reduction, which occurs at $E_p = -1.51$ V for a scan rate of 0.1 V/s. The peak current is approximately double the value obtained in the absence of CH_3I , but the electrode reaction is not catalytic as is the case for reduction of cobalt⁸ or nickel⁹ porphyrins in THF solutions containing CH_3I .

Time-resolved UV-visible spectra were obtained during controlled-potential reduction of (TPP)Ru(CO) in THF with and without added CH_3I , and examples of these spectra are given in Figure 2. Isosbestic points are located at 387, 426, 515, and 540 nm in the absence of CH_3I (Figure 2a), indicating the presence of only two spectrally detectable species in equilibrium. The final spectrum after reduction by one electron is that of the anion radical and the overall reaction corresponds to the formation of [(TPP)Ru(CO)]⁻ as shown in eq 1.^{2,3}



The spectral changes that occur in THF solutions containing CH_3I pass through two separate stages as shown in Figure 2b. At the early stage of reduction (0–60 s), the Soret and Q bands

Table I. UV-Visible Data for Neutral and Singly Reduced (TPP)Ru(CO)

solvent ^a	UV-vis data, nm		
	before redn	after redn in CH_3I soln ^b	after redn in neat solvent
THF	411, 527	407, 578	412, 446, 654, 813
DMF	413, 531	413, 581	413, 449, 665, 828
PhCN	415, 534	420, 584	421, 450, 678, 847

^aAll solvents contained 0.2 M TBAP. ^bSolutions contained 700 equiv of CH_3I .

decrease in intensity with a concomitant appearance of new bands at 578 and 598 nm. Isosbestic points are located at 393, 430, 509, and 542 nm. The Soret band continues to decrease in intensity from 1 to 4 min as the peak maximum shifts from 411 to 407 nm. At the same time, the absorbance at 578 nm continues to increase while the 598-nm band decreases and finally disappears. A new isosbestic point is observed at 590 nm during this latter stage of reduction while the other isosbestic points either shift in wavelength or disappear.

Metallophlorins are formed in reactions between reduced metalloporphyrins and methanol,^{17,18} and a similar product might be expected in solutions containing [(TPP)Ru(CO)]⁻ and CH_3I . However, this appears not to be the case since phlorin absorption bands, which are typically located above 700 nm,^{17,19} are not observed in the UV-visible spectrum of Figure 2b. On the other hand, the final UV-visible spectrum in Figure 2b has a strong absorption band at 578 nm and is characteristic of a chlorin.^{20,21}

Metallochlorens are generally easier to oxidize than metalloporphyrins by 200 to 300 mV,^{20,22,23} and a cyclic voltammogram of the isolated product further supports the conclusion of chlorin formation. The electrogenerated ruthenium(II) carbonyl methylated chlorin undergoes a reversible room temperature oxidation at $E_{1/2} = 0.87$ V in THF, 0.2 M TBAP, and this value is 260 mV more cathodic than the $E_{1/2}$ of 1.13 V for oxidation of (TPP)Ru(CO) under the same experimental conditions.

Metallochloren-type UV-visible spectra are also obtained when the reduction of (TPP)Ru(CO) is carried out in DMF or PhCN containing CH_3I . These UV-visible data are summarized in Table I. The spectra for the resulting products are similar to each other, but there is a shift of all peak maxima in DMF or PhCN with respect to values obtained in THF. This shift is consistent with an axial coordination of one or more solvent molecules to the electrogenerated product and has been previously reported for neutral (TPP)Ru(CO) under the same experimental conditions.³

The fate of the bound CO ligand after electroreduction of (TPP)Ru(CO) was ascertained by analysis of in situ FTIR spectra that were recorded before and after controlled-potential electrolysis of the complex in THF, PhCN, or DMF solutions containing CH_3I . Examples of the resulting spectra in THF are depicted in Figure 3. The initial porphyrin has a CO stretching vibration at 1941 cm^{-1} in THF (Figure 3a) and this peak shifts to 1894 cm^{-1} upon formation of [(TPP)Ru(CO)]⁻, consistent with the increased negative charge on the complex. In contrast, the 1941-cm^{-1} band of (TPP)Ru(CO) remains unchanged after reduction in THF solutions containing CH_3I (Figure 3b).

Mass Spectrometry. Twenty milligrams of (TPP)Ru(CO) was bulk electroreduced at -1.70 V in THF containing 0.1 M TBAP, after which the solution was transferred to a flask containing 20–50 equiv of CH_3I and the mixture stirred overnight. The solvent was

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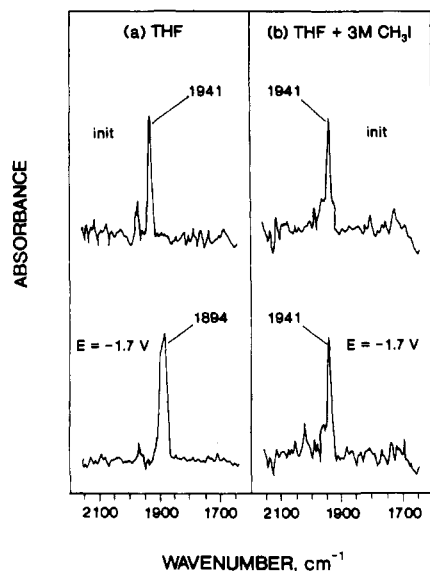


Figure 3. In situ FTIR spectra of 1.0×10^{-3} M (TPP)Ru(CO) before (top) and after (bottom) reduction at -1.70 V in THF containing 0.2 M TBAP (a) in the absence and (b) in the presence of CH_3I .

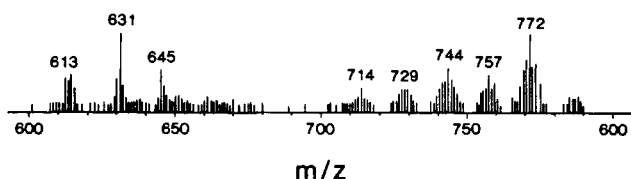


Figure 4. Mass spectrum of ruthenium(II) carbonyl tetraphenyl-dimethylchlorin.

Table II. FAB Mass Spectral Data^a

positive ion	m/z	rel abund
[TPP] ⁺	613	18
[(TPP)H ₂ + CH ₃ + H] ⁺	631	100
[(TPP)H ₂ + 2CH ₃] ⁺	645	55
[(TPP)Ru] ⁺	714	30
[(TPP)Ru + CH ₃] ⁺	729	30
[(TPP)Ru + 2CH ₃] ⁺	744 ^b	58
[(TPP)Ru(CO) + CH ₃] ⁺	757	48
[(TPP)Ru(CO) + 2CH ₃] ⁺	772	100

^aListed values with a ruthenium central metal are consistent with the ¹⁰²Ru isotope. ^bAnother possible fragment is [(TPP)Ru(CO)]⁺.

evaporated under reduced pressure, the residue dissolved in C_6H_6 , and the supporting electrolyte removed by filtration. The filtrate was then chromatographed on a silica gel column. The first eluent with C_6H_6 had a red color and was characterized as unreacted (TPP)Ru(CO). The second portion eluted with $\text{C}_6\text{H}_6/(\text{CH}_3)_2\text{CO}$ (1:1) and exhibited a green color. This band could not be further separated, and the isolated green porphyrin product was characterized by fast-atom-bombardment mass spectrometry.

The resulting mass spectrum is shown in Figure 4, and an assignment of each main fragment is listed in Table II. The highest relative abundances of the porphyrin fragments are found at mass units of 772 and 631 but the base peak (not shown) corresponds to the protonated NBA matrix and is located at $m/z = 154$. The fragment at $m/z = 772$ corresponds to the molecular ion of ruthenium(II) carbonyl tetraphenyl dimethylchlorin and the $m/z = 631$ peak to a free base tetraphenylmethylchlorin with one additional hydrogen atom.

Discussion

All of the data are self-consistent and indicate CH_3 addition to the porphyrin ring of reduced [(TPP)Ru(CO)]⁻. The resulting product is a chlorin, and this is best indicated by the electrochemical data. As earlier mentioned, one major difference between metallochlorins and metalloporphyrins is that the former species

are easier to oxidize by 200–300 mV.^{20,22,23} This is also the case for the product produced in the reaction between [(TPP)Ru(CO)]⁻ and CH_3I . The initial porphyrin is oxidized at $E_{1/2} = 1.13$ V in THF while the product of the chemical reaction is oxidized at $E_{1/2} = 0.87$ V under the same solution conditions. This magnitude of potential shift is too large to be accounted for by a simple substituent effect of the added CH_3 group, but fits well with the expected difference in $E_{1/2}$ between oxidation of a metalloporphyrin and oxidation of a metallochlorin containing the same central metal.

The similar CO frequencies of neutral and reduced (TPP)-Ru(CO) in the presence of CH_3I indicate that the CO ligand remains axially coordinated after electroreduction and that there is no significant difference between the electron density at the central metal of the initial complex and that of the final product. This result is also consistent with formation of a ruthenium(II) carbonyl chlorin and rules out formation of a Ru(III) σ -bonded methyl derivative. Published data on iron(II) carbonyl complexes of octaethylporphyrin (OEP) and octaethylchlorin (OEC) indicate that these two derivatives have virtually identical CO stretching frequencies,²⁴ and this also appears to be the case for the presently investigated porphyrin and electrogenerated chlorin.

The FAB mass spectrum in Figure 4 is well-defined, and the resulting m/z ratios indicate fragments for both metallated and demetallated CH_3 adducts. Each fragment with a Ru central metal ion appears as a cluster in the mass spectrum, and this behavior is consistent with the complex isotope pattern of the metal.²⁵ The most abundant isotope is ¹⁰²Ru and the listed m/z ratios in Table II are for fragments having this isotope.

The highest relative abundances of the porphyrin fragments are observed at $m/z = 631$ and 772 (see Table II and Figure 4) and these correspond to [(TPP)H₂ + CH₃ + H]⁺ and [(TPP)-Ru(CO) + 2CH₃]⁺, respectively. Demetallated fragments of TPP are also observed at $m/z = 613$ and 645, and this is consistent with the known demetallation of metalloporphyrins in a FAB mass spectral matrix.²⁶

The addition of CH_3 to reduced (TPP)Ru(CO) might also occur at one of the porphyrin nitrogens to give an N-substituted porphyrin.²⁷ Three strong absorption bands of N-substituted metalloporphyrins are generally located in the region 500–700 nm.²⁷ These are not observed in the UV-visible spectrum of the resulting product (see Figure 2b), and this gives additional evidence that the two methyl groups from CH_3I can only be attached to the pyrrole carbons of the porphyrin.

The addition of two methyl groups to the macrocycle of reduced (TPP)Ru(CO) can result in a mixture of cis and trans isomers, as in the case for octaethylchlorins,²⁸ or the isolated species may be a mixture of different chlorin derivatives (i.e. those with one or more methyl groups attached to the porphyrin ring). Alternatively, the isolated species might also be mixtures of different structural isomers as was discussed for the case of the α,δ -dimethyl- α,δ -dihydroporphyrin produced as a product in the reaction.²⁹ Unfortunately, the exact stereochemical orientation is not known in the present case.

In summary, this study has provided the first example for electrogeneration of a methylated chlorin. The reaction between [(TPP)Ru(CO)]⁻ and CH_3I differs from that of reduced cobalt, iron, and rhodium porphyrins in that a stable σ -bonded CH_3 derivative is not formed as a final reaction product. The first electroreduction of (TPP)Ru(CO) is clearly ring-centered,² and the electron density located at the porphyrin π -ring system favors

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an electrophilic attack to give the final chlorin product. Attempts are now underway to see if this is a general phenomenon for TPP complexes or is limited only to the case of reduced (TPP)Ru(CO).

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Two-Dimensional ^{17}O - ^{51}V Heteronuclear Shift Correlation NMR Spectroscopy of the ^{17}O -Enriched Inclusion Complex $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$. Relationship of Cross-Peak Intensity to Bond Order

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Introduction

Two-dimensional NMR experiments are invaluable for the determination of molecular structures in solution,¹ and these techniques are most frequently applied to molecules possessing ^1H and ^{13}C nuclei. However, these methods are not limited to only spin $1/2$ nuclei in organic systems, as 2-D NMR techniques have also been applied to half-integer quadrupolar nuclei ($I > 1/2$) in order to characterize the structure of inorganic clusters in solution. For example, ^{11}B - ^{11}B ($I = 3/2$) homonuclear shift correlation spectroscopy (COSY) has been used to determine B-B connectivities in polyhedral boranes² and ^{51}V - ^{51}V ($I = 7/2$) COSY experiments have yielded connectivity patterns in $\text{V}_{10}\text{O}_{32}^{6-}$ and $\text{PV}_{14}\text{O}_{42}^{9-}$.³ Furthermore, it was noted in the borane study that ^{11}B - ^{11}B COSY cross-peaks are usually absent (or very weak) for nearest-neighbor boron atoms connected by a bridging hydrogen. Thus, cross-peak intensity provides information about the bonding in borane clusters.

This work demonstrates that heteronuclear shift correlation spectroscopy (HETCOR) is also feasible for half-integer quadrupolar nuclei by applying the technique to the ^{17}O -enriched inclusion complex $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$.⁴ The results not only allow the assignment of the ^{17}O ($I = 5/2$) and ^{51}V ($I = 7/2$) NMR resonances to the known crystal structure⁴ but also provide information about the nature of the various O-V bonds in the cluster on the basis of observed cross-peak intensities.

The idealized structure of the $\text{V}_{12}\text{O}_{32}^{4-}$ cluster is represented in Figure 1. The pseudo- C_4 axis is normal to the page as indicated. The vanadium and oxygen atoms are labeled to reflect the number of distinct peaks observed in 1-D ^{51}V and ^{17}O NMR spectra⁵ that agree with the approximate C_{4h} symmetry of the cluster.⁴ The structure is like a basket with four vanadium atoms (labeled V_1) in the bottom and eight vanadium atoms (V_2 and V_3) around the rim. Every vanadium atom has a terminal oxygen bonded to it. The four vanadiums in the bottom are connected via four doubly bridging oxygens (O_2), and the eight vanadiums in the rim are connected by eight doubly bridging oxygens (O_4). The vanadiums in the rim are connected to the vanadiums in the bottom by eight triply bridging oxygens (O_3). Thus, the ^{17}O - ^{51}V HETCOR spectrum is expected to yield many cross-peaks as a result of the different types of O-V bonds.

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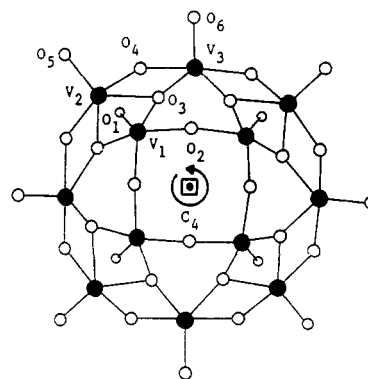


Figure 1. Idealized structure of the $\text{V}_{12}\text{O}_{32}^{4-}$ cluster showing the atom-numbering scheme. For clarity, the structure has been "flattened out". A perspective plot of the cluster can be found in ref 5.

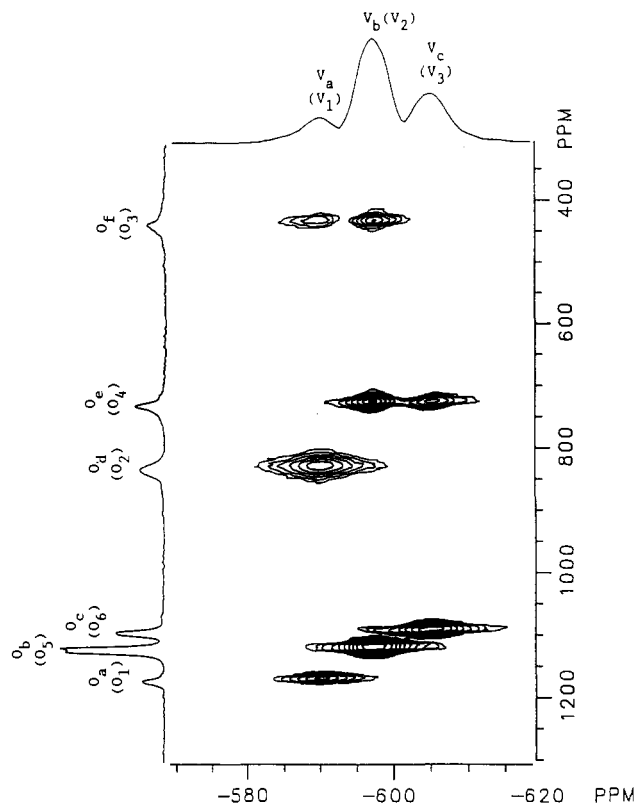


Figure 2. Contour plot of the ^{17}O - ^{51}V HETCOR NMR spectrum obtained for $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$ along with projections across the ^{17}O and ^{51}V frequency axes showing the peak-labeling scheme. Atom assignments to the structure in Figure 1 are given in parentheses.

Experimental Section

The 10% ^{17}O -enriched $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$ inclusion cluster was dissolved in CD_3CN , and the solution was transferred to a 10-mm NMR tube under nitrogen. The ^{17}O - ^{51}V HETCOR experiment⁶ was performed on a General Electric GN300WB spectrometer utilizing a custom-built 10-mm ^{17}O frequency probe (General Electric) possessing a broad-band (^{93}Nb - ^{51}V) decoupling channel. The very basic pulse sequence $[\pi/2-(^{51}\text{V})](t_1)-[\pi/2(^{51}\text{V})][\pi/2(^{17}\text{O})](t_2)$ acquire ^{17}O was used without phase cycling. The observation frequencies for ^{17}O and ^{51}V were 40.7 and 78.9 MHz, respectively. A sweep width of 62 500 Hz (dwell time 16 μs) was

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