= 3.2, J_{FF} = 16.2 Hz) and 70.3 ppm (d, J_{FF} = 16.0 Hz). The ^{19}F NMR spectrum of ethyl 3,3-difluoroacrylate[19] has signals at 64.5 ppm (dd, J_{HF} = 21.5, J_{FF} = 15.7 Hz) and 70.3 ppm (dd, J_{HF} = 2.6, J_{FF} = 15.8 Hz).[20] We believe that this is convincing chemical evidence that difluoropropadienone is indeed formed.

Other reactions of difluoropropadienone, its microwave spectrum, and its use as a source of difluorovinylidene will be reported in due course.

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The Microwave Spectrum and Molecular Structure of the Ethylene-Ozone van der Waals Complex

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We have observed a weakly bound complex between ozone and ethylene in the gas phase by using a pulsed-beam Fourier transform microwave spectrometer. The rotational constants and electric dipole moment are consistent with a structure in which the planes containing ethylene and ozone are approximately parallel. As shown in Figure 1, the centers of mass for ozone and ethylene define a line perpendicular to the two planes of length R_{cm} = 3.30 Å. It is shown below that the complex represents a small minimum on the reaction coordinate prior to the transition state which leads to the product ethylene primary ozonide (PO) depicted in Figure 2.

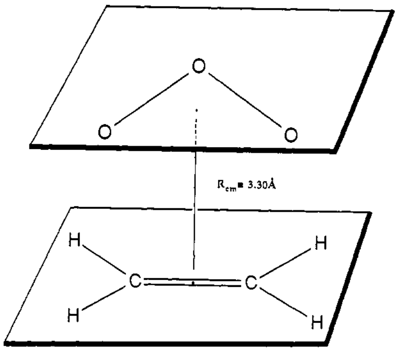

Figure 1. Approximate geometry of the ethylene-ozone complex showing the parallel planes of ethylene and ozone with a R_{cm} distance of 3.30 Å between the centers of mass of ozone and ethylene.

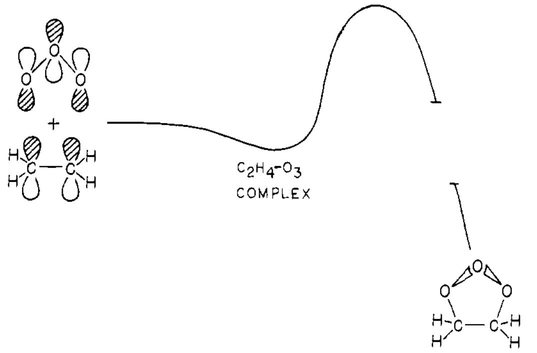

Figure 2. The reaction coordinate defined by a 1,3-dipolar cycloaddition of ozone plus ethylene producing ethylene primary ozonide through the complex observed in this work.

Table I. Rotational Transitions (MHz) of the Ethylene-Ozone Complex

transition $J'_{K_{-1},K_{+1}} - J''_{K_{-1},K_{+1}}$	ground state ν_{obsd}[a]	$\Delta\nu$[b]	excited state ν_{obsd}[a]	$\Delta\nu$[b]
$4_{04} - 3_{12}$	10 467.081	−1	10 471.375	0
$1_{10} - 0_{00}$	10 764.982	−3	10 760.404	0
$5_{05} - 4_{13}$	13 605.316	0	13 609.298	0
$5_{24} - 5_{14}$	14 450.736	0	14 441.138	−1
$4_{23} - 4_{13}$	15 569.090	0	15 559.478	2
$2_{11} - 1_{01}$	15 800.775	2	15 796.213	0
$3_{22} - 3_{12}$	16 484.367	1	16 474.752	−3
$2_{21} - 2_{11}$	17 181.317	0	17 171.717	1
$2_{20} - 2_{12}$	18 631.379	0	18 621.848	0
$3_{21} - 3_{13}$	19 466.737	−1		
$3_{12} - 2_{02}$	21 082.267	0	21 077.730	0

[a] The transition frequencies are estimated to be accurate to 4 kHz which is the resolution element. [b] $\Delta\nu$ is the observed minus calculated frequency (kHz) from the least-squares fit.

Within the context of 1,3-dipolar cycloaddition theory and Woodward-Hoffman symmetry rules, the addition of ethylene to ozone produces ethylene PO.[1,2] Overlap of the π HOMO orbital of ethylene with the π^* LUMO orbital of ozone is shown in Figure 2.[2] This parallel plane approach maintains a symmetry plane along the reaction coordinate and leads to ethylene PO in the oxygen envelope configuration. Recently, we found that the lowest energy conformation of ethylene PO is the oxygen envelope (C_s symmetry) in the gas phase.[3,4]

Two ab initio calculations find the transition-state geometry to be in accord with the parallel plane approach shown in Figure 2.[5,6] These studies indicate the transition state is more tightly bound than the complex reported here since the distance between the carbon and oxygen atoms varies from ~2.3 to ~2.0 Å in the two sets of calculations for the transition state.[5,6] One of the ab initio calculations identifies a π complex composed of ethylene bound to ozone prior to the transition state.[6] This species is weakly bound (6.2 kcal/mol more stable than ethylene plus ozone at the MP2 level dropping to only 0.9 kcal/mol in a SCF calculation).[6] While the structure is consistent with the geometry shown in

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Table II. Rotational Constants (MHz) and Centrifugal Distortion Constants (MHz) of the Ethylene–Ozone Complex[a]

	ground state	excited state
A	8246.841 (2)	8241.897 (4)
B	2518.972 (4)	2518.941 (9)
C	2044.248 (5)	2044.287 (11)
Δ_J	0.01596 (3)	0.01577 (6)
Δ_{JK}	0.2333 (2)	0.2350 (4)
Δ_K	−0.0524 (6)	−0.405 (1)
δ_J	0.00316 (2)	0.00328 (3)
δ_K	0.168 (2)	0.147 (5)

[a] Uncertainties in parentheses are one standard deviation from the least-squares fit.

Figure 1, there is some difficulty with the work since the lower level SCF computation more closely agrees with the observed 3.30 Å separation of the two planes.

The rotational spectrum was observed with a pulsed-beam FT microwave spectrometer employing a modified solenoid valve as a flow reactor. Mixtures of ~1% ozone in argon and ethylene in argon were independently passed through capillary tubing to the orifice of the pulsed valve. Optimum signals were obtained at flow rates of 200 cc/min ozone/argon and 20 cc/min ethylene/argon. Observations of argon–ozone,[7] ethylene–water,[8] and formaldehyde[9] lines during spectral searches ensured that both reactants and products were present in the pulsed supersonic jet.

The μ_c-type spectrum consisted of two sets of lines of unequal intensity split by 5–10 MHz. The rotational transitions listed in Table I were assigned using Stark effects and fit to the a-reduced I^r Watson Hamiltonian.[10] Table II gives the spectral constants obtained from these fits of the two states. The electric dipole moment was determined to be $\mu_c = 0.461$ (2) D from Stark shift measurements of the 2_{11}–1_{01} and 1_{10}–0_{00} transitions for both states. This compares to a value of 0.532 (3) D measured for ozone.[11]

The structure that is consistent with the electric dipole and inertial moment data is shown in Figure 1. This geometry gives (in MHz) $A = 8030$, $B = 2518$, and $C = 2044$. Small rotations (about 30°) of the ethylene and ozone planes which maintain C_s symmetry produce a small nonzero projective μ_a dipole component and better agreement between the calculated and observed A rotational constant. However, additional isotopic moment data are needed to determine the oxygen to carbon distances and whether or not the two planes are parallel.

The identification of two sets of lines suggests a tunneling motion is present in the complex. It is likely that the states arise from internal rotation rather than inversion since the μ_c-type transitions fit well to a Watson Hamiltonian. An observed intensity ratio of ~2:1 for the two states is consistent with the 10:6 nuclear spin statistics expected for internal rotation of ethylene about its C_2 axis.[12] The small splitting of the two sets of transitions means the barrier hindering internal rotation must be substantial.

Recent microwave work on the ethylene–SO_2 complex shows that the molecular structure and internal motion are similar to the ethylene–ozone complex.[13,14] In both cases additional isotopic data are required to better understand the internal motions present in these complexes.

Acknowledgment is made to Prof. R. L. Kuczkowski for helpful comments related to the 1,3-dipolar cycloaddition theory.

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Mixed-Valent Octanuclear Platinum Acetamide Complex, $[Pt_8(NH_3)_{16}(C_2H_4NO)_8]^{10+}$

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Since the first structural study of a platinum blue with α-pyridonate ligands in 1977,[1] several platinum blue related complexes have been synthesized and structurally clarified, all of them with cyclic amidate ligands.[2-6] In these platinum blues, the tetraplatinum chain structure is achieved by a metal–metal interaction only between O,O-coordinated Pt atoms of amidate-bridged head-to-head dimers. Other interactions between N,N- or N,O-coordinated Pt atoms are prevented due to the steric hindrances of cyclic amidate rings. However, the classical "platin blaus" were synthesized with chain amides,[7] which have no steric bulks at their N positions. In the present study, acetamide is selected as the bridging ligand expecting other interdimer interactions than between O,O-coordinated Pt atoms. We report the first octanuclear platinum chain complex, unveiling the structure of a chain amidato platinum blue never solved before.

The complex was synthesized from an aqueous solution of *cis*-diammineplatinum(II) hydrolysis product (3 mmol/21 mL).[8] A blue-purple solution ($\lambda_{max} = 540$ nm) of the complex was obtained by heating the solution with equimolar acetamide at 70 °C for 3 h. Gradual concentration of the solution was made at 5 °C to form red-purple plate crystals of the complex $[Pt_8(NH_3)_{16}(C_2H_4NO)_8](NO_3)_{10}{\cdot}4H_2O$.[9]

An ORTEP view for the structure of the complex is shown in Figure 1 with its selected Pt–Pt distances and angles.[10] The most remarkable structural feature is that the complex cation is octanuclear, with a crystallographic inversion center at its molecular center. The octameric unit consists of four dimeric units, each doubly bridged with acetamidate ligands in a head-to-head manner, with three interdimer interactions. The inner tetrameric unit has a structure quite similar with those of typical tetranuclear platinum (2.0+,[5] 2.25+,[1,2] and 2.5+[4]) blues. The central interdimer interaction of Pt(4)–Pt(4′) = 2.934 (1) Å is reinforced by four hydrogen bonds between oxygens of acetamidates and ammines (O(3)–N(12′) = 2.85 (3) Å and O(4)–N(11′) = 2.80 (3)

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(9) Anal. Calcd for $Pt_8O_{42}N_{34}C_{16}H_{88}$: C, 6.43; H, 2.97; N, 15.93. Found: C, 6.60; H, 2.77; N, 15.49.

(10) Crystallographic data: $Pt_8O_{42}N_{34}C_{16}H_{88}$, triclinic $P\bar{1}$, $a = 12.091$ (2) Å, $b = 13.557$ (3) Å, $c = 10.983$ (4) Å, $\alpha = 100.62$ (2)°, $\beta = 97.12$ (2)°, $\gamma = 89.79$ (2)°, $V = 1755.5$ Å^3, $Z = 1$, D(calcd) = 2.828 g/cm^3, $\mu = 161.5$ cm^{-1}. Of 6345 reflections collected (Rigaku AFC-5R, 25 °C, Mo Kα, 2θ(max) = 50°, $\pm h$, $\pm k$, l), 5547 were independent, and 5063 ($F_o > 4\sigma(F_o)$) were used for the calculation. Analytical deterioration and absorption corrections were applied to the data. The structure was solved by direct method (MULTAN). All the calculations were performed with the UNICSIII program. All nonhydrogen atoms were treated anisotropically. Only structurally important hydrogen atoms at each N position of acetamidates were located in the difference synthesis and refined isotropically. $R(R_w) = 0.055$ (0.086), $w = 1/\sigma^2(F_o)$ for 468 refined parameters, GOF = 2.68, $\Delta(\rho)_{max} = 1.83$ e/Å^3 (except peaks 1.06 Å around Pt atoms).

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