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.

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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 (λ_{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, α = 100.62 (2)°, β = 97.12 (2)°, γ = 89.79 (2)°, V = 1755.5 Å^3, Z = 1, D(calcd) = 2.828 g/cm^3, μ = 161.5 cm^{-1}. Of 6345 reflections collected (Rigaku AFC-5R, 25 °C, Mo Kα, 2θ(max) = 50°, ±h, ±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 non-hydrogen 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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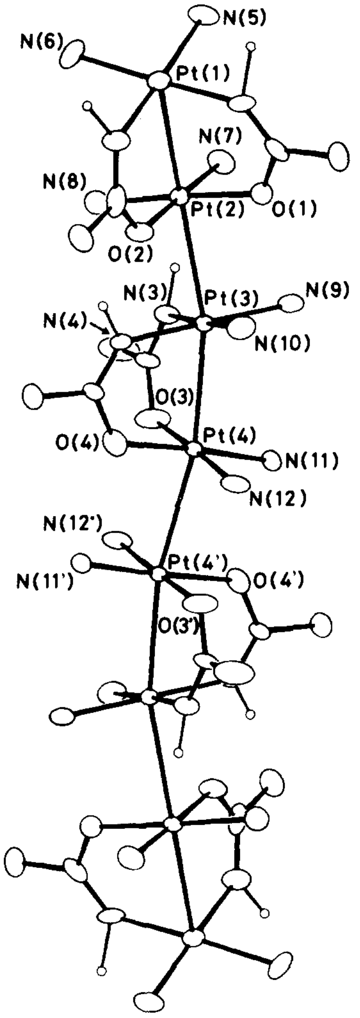
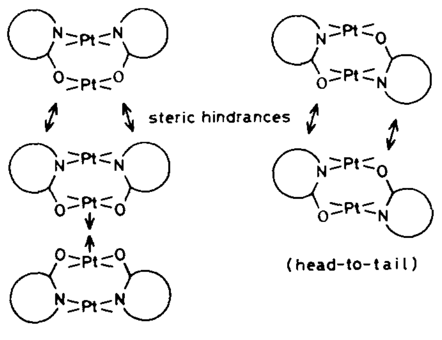


Figure 1. ORTEP view of the $[Pt_8(NH_3)_{16}(C_2H_4NO)_8]^{10+}$ cation. Selected Pt–Pt distances (Å) and angles (deg) are as follows: Pt(1)–Pt(2), 2.880 (2); Pt(2)–Pt(3), 2.900 (1); Pt(3)–Pt(4), 2.778 (1); Pt(4)–Pt(4'), 2.934 (1); Pt(1)–Pt(2)–Pt(3), 163.77 (5); Pt(2)–Pt(3)–Pt(4), 165.51 (4); Pt(3)–Pt(4)–Pt(4'), 168.78 (5), where a symmetry operation for Pt(4') is -*X*, -*Y* + 1, -*Z* + 1.

Scheme I



Å). Each outer interdimer interaction of Pt(2)–Pt(3) = 2.900 (1) Å is also reinforced by two chemically nonequivalent hydrogen bonds (O(1)–N(10) = 2.98 (3) Å and O(2)–N(4) = 2.83 (3) Å), where a new type of interdimer interaction is achieved between the outer O,O-coordination and the inner N,N-coordination spheres. The close contacts of non-hydrogen-bonding nitrogens between Pt(2) and Pt(3) planes, N(8)–N(3) = 3.26 (4) Å and N(7)–N(9) = 3.45 (4) Å, and the large torsional angle of 37.9° about the Pt(2)–Pt(3) axis suggest an attractive interaction of the two planes. Both of the interdimer Pt–Pt distances are a little longer than the values of 2.866 (2)–2.9158 (6) Å for the tetranuclear platinum (2.25+) blues,[1,2] but still much shorter than the values of 3.129 (1)–3.2355 (5) Å for the tetranuclear $Pt(II)_4$ complexes.[5] Table I summarizes geometric features around Pt–Pt vectors.

Table I. Geometric Features around the Pt–Pt Spheres

Pt–Pt	τ,[a] deg	ω,[b] deg	repulsion distances,[c] Å (esd)
Pt(1)–Pt(2)	28.4	3.7	N(5)–N(7) = 3.66 (4), N(6)–N(8) = 3.68 (4)
Pt(2)–Pt(3)	10.7	37.9	N(7)–N(9) = 3.45 (4), N(8)–N(3) = 3.26 (4)
Pt(3)–Pt(4)	25.6	5.6	N(9)–N(11) = 3.57 (4), N(10)–N(12) = 3.47 (3)

[a] Tilt angles between adjacent platinum coordination planes. [b] Average torsional angles about the Pt–Pt axes. [c] Repulsion distances between nonbridged ammines, including a non-hydrogen-bonded nitrogen of acetamidate, N(3).

As the unit cell contains ten nitrate anions, the average platinum oxidation state is 2.25, $Pt^{II}_6Pt^{III}_2$. The complex shows no ESR signal and seems to be diamagnetic. The intradimer Pt–Pt distances are different between the inner (2.778 (1) Å) and the outer (2.880 (2) Å) dimers. The former, 2.778 (1) Å, is comparable to the values of 2.7745 (4)[1b] to 2.8296 (5)[2] Å for the tetranuclear platinum (2.25+) blues, suggesting the average oxidation state for the inner units is close to 2.25, and, therefore, the outer two units would also be partially oxidized. Since there are no distinctively short distances ascribable to Pt(II)–Pt(III)[4] or Pt(III)–Pt(III),[6] all seven Pt–Pt distances would be rather equivalent except for the existence or the absence of the bridging ligands. Therefore, it seems probable that the two Pt(III) states delocalize over several Pt atoms as in the previous platinum blues.

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Supplementary Material Available: Tables giving crystallographic data, positional parameters, mean square displacement tensors, symmetry operations, bond distances and angles, torsion angles, shifts of Pt atoms from the least-squares planes, dihedral angles between Pt coordination planes, and repulsion distances (14 pages); listing of structure factors (26 pages). Ordering information is given on any current masthead page.

A Remarkable Effect of Solvent Size on the Stability of a Molecular Complex

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The thermodynamic stability of molecular complexes depends in part upon attractive forces between the binding partners and upon changes in entropy which occur on binding. It also depends upon solvation. For organic molecules dissolved in organic solvents, solvation energies are usually negative, and the decreases in solvation which often accompany binding inhibit molecular complex formation. An example of such a phenomenon is provided by the solvent-dependent dimerization of the five-membered lactam 2-pyrrolidinone. In CCl_4, the lactam forms a hydrogen-bonded dimer with a dissociation energy of ~3 kcal/mol which falls to 0.0–0.6 kcal/mol in the more polar, hydrogen bond donor solvent $CHCl_3$.[1,2] The decrease in dissociation energy which occurs on

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