Obviously, the other ESA bands are considerably more intense. Similar intensity discrepances between excited-state and ground-state spectra have been noted[2] in the case of $Co(CN)_6^{3-}$. Probably in the ESA spectrum the vibronic mechanism of d–d intensity is more effective due to the vicinity of strongly allowed LMCT or d–p bands.

In conclusion, a ligand field analysis seems to confirm kinetic evidence for the ESA nature of the reported transient spectrum. Reasonable estimates of the prominent ESA peaks could be obtained by taking the Stokes shift as a measure for the decrease in ligand field strength upon relaxation to the metastable state.

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Chemical Applications of Topology and Group Theory. 18. Polyhedral Isomerizations of Seven-Coordinate Complexes[1]

R. B. King

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A topic of considerable interest to inorganic chemists is the stereochemical nonrigidity in ML_n coordination complexes (M = central atom, generally a metal; L = ligands surrounding M). Several theoretical approaches have been used to study such stereochemical nonrigidity. Thus, selected types of possible isomerizations of ML_n polyhedra [n = 4,[2] 5,[3] 6,[4] and 8[5]] have been represented topologically[2,6] as graphs in which the vertices represent different polyhedral isomers and the edges represent possible one-step isomerizations. Selected individual polyhedral isomerizations have been described in terms of processes originally called diamond–square–diamond (dsd) processes[7] but can be more systematically called 4-pyramidal processes.[8] A recent paper of this series[8] used Gale transformations[9] to find all possible nonplanar isomerization processes for polyhedra having five and six vertices. By this approach all degenerate nonplanar isomerizations of five-vertex polyhedra were shown to be formulated as sequences of Berry pseudorotation processes, the prototypical dsd or 4-pyramidal process. Furthermore, study of the Gale transformations reveals that degenerate nonplanar isomerizations of the seven combinatorially distinct six-vertex polyhedra can be expressed in terms of six distinct types of 4-pyramidal processes and the two prototypical 5-pyramidal processes.

The success of the Gale transformation approach for the study of polyhedral isomerizations lies in the ability of Gale transformations to reduce the dimensionality of the problem. Thus, the Gale transform of a (three-dimensional) polyhedron having v vertices can be imbedded into (v–4)-dimensional space.[8] The Gale transform of a tetrahedron is thus a single point, the Gale transform of a five-vertex polyhedron (trigonal bipyramid or square pyramid) consists of points on a line, and the Gale transform of any of the seven six-vertex polyhedra consists of points in a plane. This dimensionality reduction is the key to the value of Gale transforms in the study of isomerizations of polyhedra with "few" vertices[9] (i.e., ≤6 vertices).

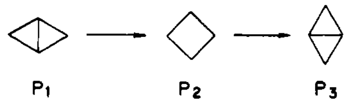
Polyhedra having more than six vertices are also of interest to inorganic chemists. However, Gale transformations offer no advantage for the study of the isomerizations of such polyhedra since they no longer provide dimensionality reduction (i.e., for $v > 6$, $v-4 \geq 3$). However, the experience provided by the Gale transformation study of five- and six-vertex polyhedra[8] coupled with the still manageable number of combinatorially distinct seven-vertex polyhedra, namely 34,[10] allows an exhaustive study of isomerizations of seven-vertex polyhedra. This paper summarizes the results of such a study. Polyhedra having seven vertices are of interest in representing the coordination polyhedra of the large variety of known ML_7 complexes.[11]

Background

A polyhedral isomerization step may be defined[6] as a deformation of a specific polyhedron P_1 to the point that the vertices define a new polyhedron P_2. Of particular interest in the context of this work are sequences of two polyhedral isomerization steps $P_1 \rightarrow P_2 \rightarrow P_3$ with the following properties: (a) P_3 has the same number of edges as P_1. (b) P_2 has one less edge than P_1 (or P_3). Such a polyhedral isomerization can be considered to result from removal of one edge from P_1 to give P_2 followed by adding the edge back to P_2 in a different way to give P_3. Note that by definition all polyhedra involved in a sequence of isomerization steps must have the same number of vertices. If P_1 and P_3 are combinatorially equivalent, the polyhedral isomerization $P_1 \rightarrow P_2 \rightarrow P_3$ is called a *degenerate* polyhedral isomerization.

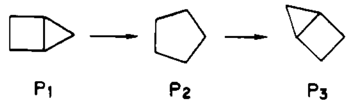
Let us now consider the effects of edge removal from P_1 on the face structure of the resulting polyhedron P_2. Removal of a single edge will convert two faces into a single larger face, which can be called the *pivot* face. If the pivot face has n edges, then the process $P_1 \rightarrow P_2 \rightarrow P_3$ defined as above will be an n-pyramidal process. Note that, for rearrangements of polyhedra having v vertices, the admissible values for n are $4 \leq n \leq v$. A v-pyramidal polyhedral isomerization of a v-vertex system is a *planar* polyhedral isomerization since the intermediate "polyhedron" P_2 is actually a planar polygon with v vertices.

These concepts may be illustrated more concretely. A 4-pyramidal process involves removal and subsequent addition of an edge in the following way so that P_1 and P_3 have the same number of edges:



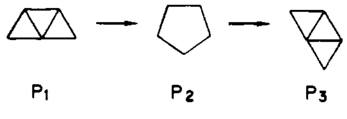
(1)

This, of course, is the familiar dsd process.[7,12] A 5-pyramidal process merges adjacent triangle and quadrilateral faces into a pentagonal face in the intermediate polyhedron P_2 as follows:



(2)

An example of this type of process is described in the Gale diagram paper.[8] The 4-pyramidal and 5-pyramidal processes (1) and (2) can be combined to give the following process:



(3)

In this process (eq 3), *two* edges are removed from P_1 to give P_2 and those two edges are added back to P_2 in a different way to

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give P_3. Such a combination of an *m*-pyramidal and an *n*-pyramidal process where $n > m$ is conveniently classified as an *n*-pyramidal process since the intermediate polyhedron P_2 has a pivot face having *n* edges.

This paper also considers parallel polyhedral isomerization processes. In a parallel process two or more *equivalent* edges are removed from P_1 to give P_2 and the same number of edges are added in a different way to equivalent sites of P_2 to give P_3. Examples of parallel processes include the double dsd interconversion of two eight-vertex D_{2d} dodecahedra through a square-antiprismatic intermediate[5] and the triple dsd interconversion of two six-vertex octahedra through a trigonal-prismatic intermediate (the "Bailar twist").[13]

The total number of possible rearrangements for polyhedra having *v* vertices can rapidly become unmanageably large with increasing *v* even for cases where *v* is still of chemical interest. Energetic and symmetry considerations can be used to select rearrangements of specific interest in a chemical context. Thus, rearrangements $P_1 \rightarrow P_2 \rightarrow P_3$ involving a pivot face in P_2 having a minimum number of edges are energetically favored since a minimum number of ligands need to approach coplanarity in the intermediate polyhedron P_2. A large number of coplanar ligands is definitely unfavorable in terms of interligand repulsion and in extreme cases (≥6 coplanar ligands) may require impossible atomic orbital hybridizations. Such energetic considerations make polyhedral isomerizations involving dsd processes the most energetically favorable in accord with the remarkable insight of Lipscomb nearly 20 years ago.[7] Similar considerations lead to exclusion of *planar* polyhedral isomerizations for energetic reasons. Use of such energetic considerations appears to be sufficient to reduce the number of interesting rearrangements of seven-vertex polyhedra to a manageable number. However, use of a similar approach to study rearrangements of eight-vertex polyhedra will undoubtedly require not only such energetic considerations but also restriction to polyhedral systems having certain symmetry since otherwise the total number of combinatorially distinct eight-vertex polyhedra is an unmanageable 257.[10]

In exploration of relatively large numbers of seven-vertex polyhedral isomerizations, it has proven most convenient to consider first the intermediate polyhedra P_2 in rearrangements of the type $P_1 \rightarrow P_2 \rightarrow P_3$. Such polyhedra must necessarily have at least one nontriangular face and can conveniently be called *non-deltahedra.* The five seven-vertex deltahedra thus cannot be intermediate polyhedra P_2 in polyhedral rearrangements. This reduces the number of possible seven-vertex intermediate polyhedra to the 29 seven-vertex non-deltahedra. Furthermore, one of these non-deltahedra, namely the hexagonal pyramid, can be the intermediate polyhedron only in energetically unfavorable 6-pyramidal processes. For the remaining 28 seven-vertex non-deltahedra it is feasible to draw diagonals across the non triangular faces in all possible ways, thereby generating all possible transformations $P_1 \rightarrow P_2$ and $P_2 \rightarrow P_3$ involving the non-deltahedron in question as P_2. If two different ways of drawing diagonals (conveniently called *diagonalization*) across the nontriangular faces of a given non-deltahedron lead to combinatorially equivalent polyhedra P_1 and P_3, then the non-deltahedron in question can serve as the intermediate polyhedron P_2 in a *degenerate* isomerization $P_1 \rightarrow P_2 \rightarrow P_3$.

Results

Federico[10] has described the properties of the 34 combinatorially distinct polyhedra having seven faces. These polyhedra P_i can be converted to their duals[9] P_i^* by the following process: (1) The vertices of P_i^* are located at the midpoints of the faces of P_i. (2) Two vertices of P_i^* are connected by an edge if and only if the corresponding faces of P_i share an edge. The duals of the 34 polyhedra having seven faces are the 34 possible combinatorially distinct polyhedra having seven vertices.

The properties of these 34 seven-vertex polyhedra are listed in Table I, including the following for each polyhedron: (1) the number of the dual in Federico's paper[10] so that readers can relate material in this paper to that earlier work (Federico's paper contains the Schlegel diagrams[9] of all of the polyhedra having seven faces); (2) the degrees of the vertices (vertex index) expressed as a four-digit number $v_6v_5v_4v_3$ where v_n is the number of vertices of degree *n*; (3) the sizes of the faces (face index) expressed as a four-digit number $f_6f_5f_4f_3$ where f_n is the number of faces having *n* edges (and *T* is used as a digit for 10); (4) the symmetry point group;[14] (5) other distinctive features such as the number of edges of a particular type where e_me_n means an edge connecting a vertex of degree *m* with one of degree *n*.

All of the non-deltahedra in Table I have been investigated as intermediate polyhedra P_2 for polyhedral rearrangements of the type $P_1 \rightarrow P_2 \rightarrow P_3$. This has been done by the diagonalization process described in the previous section; i.e., all possible diagonals have been drawn across vertices of nontriangular faces, and the resulting polyhedra have been determined (and in Table I are indexed according to the Federico number). For non-deltahedra having only triangular and quadrilateral faces, the number of different ways of drawing such diagonals is $2f_4$ where f_4 is the number of quadrilateral faces. For non-deltahedra having pentagonal faces (E in Table I), only diagonalization of the pentagonal face has been considered in Table I since diagonalization of a pentagonal face is assumed to be energetically more favorable than diagonalization of a quadrilateral face. There are five different ways of drawing a diagonal across a pentagonal face to split the pentagonal face into a triangular and a quadrilateral face.

A non-deltahedron P_2 can be the intermediate polyhedron in a *degenerate* polyhedral isomerization $P_1 \rightarrow P_2 \rightarrow P_3$ (P_1 and P_3 are combinatorially equivalent; P_2 has one less edge than P_1 or P_3) if and only if two or more different ways of diagonalizing a nontriangular face of P_2 lead to the same polyhedron corresponding to P_1 in one case and P_3 in the other case. If the nontriangular face of P_1 being diagonalized is quadrilateral, such an isomerization is a single dsd process. Such degenerate isomerizations are not particularly common and therefore are starred in Table I. Interestingly only one of the five seven-vertex deltahedra, namely the low-symmetry (C_2) #13, can undergo degenerate isomerization through a single dsd process. The other seven-vertex deltahedra require multiple dsd processes or energetically relatively unfavorable 5-pyramidal or 6-pyramidal processes for their degenerate polyhedral isomerizations.

These considerations allow one to define a *dsd rigidity index* of a polyhedron P_1 as the number of edges that must be removed from P_1 in a dsd manner (i.e., converting two adjacent triangular faces into a single quadrilateral face) in order to give an intermediate polyhedron P_2, which upon adding back the same number of edges gives a polyhedron P_3 combinatorially equivalent to P_1; i.e., $P_1 \rightarrow P_2 \rightarrow P_3$ is a degenerate isomerization involving only dsd processes. Four of the five seven-vertex deltahedra including the chemically significant[11] pentagonal bipyramid and capped octahedron have a dsd rigidity index of 2 which means that a degenerate isomerization must involve loss of two edges to give an intermediate polyhedron having two quadrilateral faces. Four of the 28 seven-vertex polyhedra having only triangular and quadrilateral faces cannot undergo degenerate isomerizations involving only dsd (4-pyramidal) processes and therefore have a dsd rigidity index of 0. The degenerate isomerization of such polyhedra must involve less energetically favorable *n*-pyramidal ($n \geq 5$) processes. None of the seven-vertex polyhedra having a dsd rigidity index of 0 have been found to be chemically significant.

The relationships between dsd processes involving seven-vertex deltahedra are depicted in the *dsd graphs* shown in Figure 1. The vertices of the dsd graphs represent seven-vertex polyhedra designated by the Federico numbers of their duals as given in Table I. The edges of the dsd graph represent a "diamond-square" ($P_1 \rightarrow P_2$ in (1) above) or a "square-diamond" ($P_2 \rightarrow P_3$ in (1) above) isomerization step in a dsd process depending upon the direction

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Table I. Some Important Properties of the 34 Seven-Vertex Polyhedra

Federico no. of dual[a]	vertex index[b]	face index[c]	sym	dsd rigidity index[d]	polyhedra formed by diagonalization	distinctive features[f]
(A) Deltahedra						
#11	2032	000*T*	C_{2v}	2		$2v_6$
#12	1303	000*T*	C_{3v}	2		$1v_6 + C_3$ axis
#13	1222	000*T*	C_2	1		$1v_6 + C_2$ axis
#20	0331	000*T*	C_{3v}	2		capped octahedron
#23	0250	000*T*	D_{5h}	2		pentagonal bipyramid
(B) Polyhedra with One Quadrilateral Face						
#14	1123	0018	C_s	2	#11, #12	0 e_{33}
#15	1123	0018	C_1	1	#11, #13	1 e_{33}
#16	1042	0018	C_{2v}	2	#13*	
#21	0313	0018	C_s	2	#13*	3 e_{45}
#22	0313	0018	C_s	1	#11, #23	2 e_{45}
#24	0232	0018	C_s	2	#11, #23	0 e_{55}
#25	0232	0018	C_1	1	#13, #20	1 e_{55}
#28	0151	0018	C_s	1	#20, #23	
(C) Polyhedra with Two Quadrilateral Faces						
#18	1024	0026	C_{2v}	2	#15*	
#26	0214	0026	C_1	2	#14, #15, #22, #25	2 connected e_{33}
#27	0214	0026	C_2	0	#15*, #22*	2 disconnected e_{33}
#30	0133	0026	C_2	1	#22*, #28*	1 e_{44}
#31	0133	0026	C_s	2	#14, #22, #24, #28	2 e_{44}
#32	0133	0026	C_1	1	#16, #21, #25*	2 e_{44}
#33	0133	0026	C_1	1	#15, #24, #25, #28	3 e_{44}
#36	0052	0026	C_{2v}	1	#28*	4-capped-trigonal prism (1 e_{33})
#37	0052	0026	C_2	2	#25*, #28*	0 e_{33}
(D) Polyhedra with Three or Four Quadrilateral Faces						
#35	0115	0034	C_s	1	#18, #26, #30, #33	
#39	0034	0034	C_{3v}	0	#32*	3-capped-trigonal prism, self-dual
#40	0034	0034	C_{3v}	1	#30*, #36*	self-dual
#41	0034	0034	C_2	0	#27, #32*, #33*, #37	self-dual
#42	0034	0034	C_1	1	#26, #30, #31, #33, #36, #37	$1v_3$ surrounded by $3v_4$, self-dual
#44	0016	0042	C_{2v}	0	#35*, #40*, #42*	4 quadrilateral faces
(E) Polyhedra with Pentagonal or Hexagonal Faces						
#17	1024	0107	C_s	1	#14*, #15*, #16	3-capped pentagonal pyramid
#29	0133	0107	C_s	1	#22, #25*, #28*	
#34	0115	0115	C_1	1	#26, #27, #30, #31*	self-dual
#38	0034	0115	C_s	1	#32*, #36, #37*	
#43	0016	0123	C_s		#39, #41*, #42*	
#19	1006	1006	C_{6v}		#11*, #12*, #13*, #14*, #17*, #18*	hexagonal pyramid

[a] These numbers are the same as those given in Table I of: Federico, P. J. *Geom. Ded.* **1975**, *3*, 469. [b] The vertex index corresponds to $v_6v_5v_4v_3$ where v_n is the number of vertices of degree *n* (see text). [c] The face index corresponds to $f_6f_5f_4f_3$ where f_n is the number of faces with *n* edges and the letter *T* is used as a digit for 10. [d] The dsd rigidity index is defined in the text. [e] The polyhedra formed by drawing all possible diagonals on nontriangular faces are indicated by the Federico numbers of their duals (note (a) and text). Combinatorially equivalent polyhedra formed by two or more different diagonalization processes are starred. These correspond to *degenerate* pyramidal isomerization processes. [f] Distinctive features include special names for the polyhedra, the presence or absence of vertices (v_n) or edges (e_me_n) of distinctive types, and/or self-duality. The edge designation e_me_n refers to an edge connecting a vertex of degree *m* with one of degree *n*.

the edge is traversed. Vertices on the left of these dsd graphs represent seven-vertex deltahedra having 10 triangular faces (i.e., Federico numbers #11, #12, #13, #20, and #23), vertices in the center of these dsd graphs represent seven-vertex polyhedra having eight triangular faces and one quadrilateral face (i.e., Federico numbers #14, #15, #16, #21, #22, #24, #25, and #28), and vertices on the right of these dsd graphs represent seven-vertex polyhedra having six triangular and two quadrilateral faces (i.e., Federico numbers #18, #26, #27, #30, #31, #32, #33, #36, and #37). Degenerate *single* dsd processes (i.e., those corresponding to starred polyhedra in the diagonalization column of Table I) appear as double edges in the dsd graphs. Degenerate double dsd processes are circuits of length 4, including a left vertex corresponding to the starting deltahedron. In formation of these circuits only a double edge can be traversed twice; a single edge can only be traversed once.

The dsd graphs in Figure 1 clearly indicate the dsd rigidity index of 1 for the C_2 deltahedron #13 (i.e., through #16 or #21 as an intermediate) and the dsd rigidity indices of 2 for the other four seven-vertex deltahedra including the chemically significant pentagonal bipyramid (#23) and the capped octahedron (#20). Of particular interest are the degenerate double dsd isomerizations of these two polyhedra through the route #20 or #23 → #28 → #36 → #28 → #20 or #23 since the intermediate polyhedron #36 is the capped-trigonal prism, which is a chemically significant non-deltahedral seven-vertex coordination polyhedron[11] with six triangular and two quadrilateral (rectangular) faces. In the case of degenerate isomerization of the pentagonal bipyramid, the subtraction of two edges to form the capped-trigonal prism intermediate and the subsequent addition of two edges to re-form a combinatorially equivalent pentagonal bipyramid can each be viewed as concerted processes so that the symmetry of this system never falls below the C_{2v} symmetry of the capped-trigonal prism. This is a good example of two parallel dsd processes and is feasible since the C_{2v} point group of the capped-trigonal prism is a subgroup of the D_{5h} point group of the pentagonal bipyramid. A similar concerted view of the degenerate double dsd isomerization of a capped octahedron through a capped-trigonal-prismatic intermediate is not feasible since the two edges of the capped octahedron that are removed to form a capped-trigonal prism are nonequivalent. This is a consequence of the fact that the C_{2v} point group of the capped-trigonal prism is not a subgroup of the C_{3v} point group of the capped octahedron. Despite the attractiveness of the degenerate isomerizations of the pentagonal bipyramid and the capped octahedron through capped-trigonal-prismatic intermediates because of the relatively high symmetry of the key

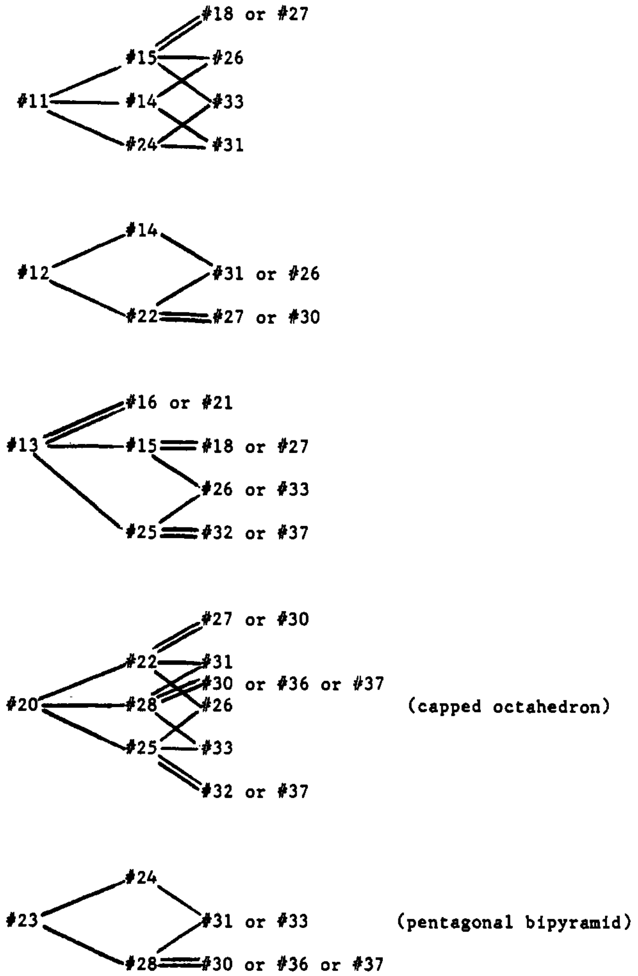

Figure 1. dsd graphs for 7-vertex deltahedra.

polyhedra and the chemical significance of the intermediate polyhedron, Figure 1 indicates a variety of other possible dsd processes for the degenerate isomerization of the pentagonal bipyramid and the capped octahedron. Distinguishing between these diverse dsd processes is likely at best to be extremely difficult experimentally, although differences in symmetry might be exploited in very carefully designed low-temperature NMR experiments on specially constructed systems in order to obtain some relevant information.

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Activation Parameters and Mechanism for Water Exchange of Tetraaquaplatinum(II) Studied by High-Pressure Oxygen-17 NMR Spectroscopy[1]

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Solvent-exchange reactions at metal ions are fundamental for the understanding of complex formation and some redox reactions. Although substitution reactions of square-planar complexes have been extensively investigated, only two studies of their solvent exchange seem to have been published so far.[4,5] Platinum-195 NMR was recently used to follow the kinetics of water exchange of $Pt(H_2O)_4^{2+}$.[4] Similar rates for entry of water and dimethyl sulfoxide and for transfer of a chloride ligand from $HgCl^+$ to $Pt(H_2O)_4^{2+}$ were found, and the approximate activation entropies for the water exchange and the entry of dimethyl sulfoxide were slightly positive. Those observations led to the conclusion that the intimate mechanism of substitution in $Pt(H_2O)_4^{2+}$ might change from I_a to I_d for those entering ligands.[4] On the other hand, dimethyl sulfide exchange of *trans*-$Pd(Me_2S)_2Cl_2$, studied by proton NMR spectroscopy, has negative entropies and volumes of activation, compatible with an associative activation for the exchange.[5]

A more comprehensive investigation of the water exchange of $Pt(H_2O)_4^{2+}$, including a variable-pressure study, seemed very desirable in view of these results. Since up to 0.5 M solutions of the complex can now be prepared,[6] the slow water exchange at $Pt(H_2O)_4^{2+}$ can be followed with good accuracy by use of the increase in height of the oxygen-17 NMR signal from coordinated water obtained when platinum(II) perchlorate solutions are mixed with oxygen-17-enriched water. We report here the result of such studies.

Experimental Section

Chemicals and Solutions. Ca. 10 mM solutions of tetraaquaplatinum(II) perchlorate in aqueous perchloric acid (1.00 M; Baker p.a.) were prepared from potassium tetrachloroplatinate(II) (Johnson and Matthey) and anhydrous silver perchlorate (G. F. Smith, reagent quality) as described previously.[6,7] These solutions were concentrated by repeated evaporation, partial neutralization of excess acid with potassium hydrogen carbonate (Merck p.a.), and separation of excess perchlorate as the potassium salt. Further details are given elsewhere.[6] The procedure gave platinum stock solutions (10–15 mL) for the NMR experiments, with the following concentrations of $[Pt(H_2O)_4](ClO_4)_2$ and $HClO_4$, respectively: 0.549, 3.31 *m*; 0.581, 3.51 *m*; 0.580, 3.60 *m*. The stock solutions were kept under nitrogen in a refrigerator. Their UV spectra agreed with those published for other concentrated platinum(II) perchlorate solutions.[6] Polynuclear hydrolysis was negligible. The solutions were analyzed for perchloric acid by use of a glass electrode, and platinum concentrations were determined spectrophotometrically at 275 nm, where the molar absorptivity of $Pt(H_2O)_4^{2+}$ is 56.5 cm^{-1} M^{-1}.[7] Distilled oxygen-17-enriched water (8–20 atom %, normalized in ^1H) was from Yeda.

Instrumentation. All oxygen-17 NMR spectra were recorded on a Bruker CXP-200 spectrometer equipped with a 4.7-T wide-bore cryomagnet working at 27.11 MHz. The accumulated free-induction decays were stored on a DIABLO hard disk system. The temperature was held constant within ±0.3 °C by flushing air or nitrogen through the probe. It was measured by a substitution technique using a platinum resistor.[8] Exchange rate measurements under pressure were performed at 297 K with a high-pressure probe described elsewhere.[9] For fast exchange at higher temperatures, a fast-injection apparatus was used. It is described elsewhere.[10] Absorption spectra were recorded by use of Cary 14 and Perkin-Elmer Hitachi 340 instruments.

NMR Measurements. The water exchange was followed by mixing weighed quantities (ca. 0.5–0.8 g for measurements at ambient pressure; ca. 1.3–1.6 g for high-pressure measurements) of platinum stock solutions and oxygen-17-enriched water and recording the NMR spectra as a function of time. Accumulation time for a single spectrum varied between 1200 and 12.9 s for measurements at ambient pressure, depending on the exchange rate, and was 240 s for the high-pressure measurements. Further details are given in the captions of Figures 1 and 2.

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