Reactions of Nitroplatinum Complexes. 2. Reactions of $K_2[Pt(NO_2)_4]$ and Related Complexes with Aqueous Acids (CH_3CO_2H, $HClO_4$, CF_3SO_3H, HNO_3, and H_2SO_4): Pathways to Platinum(III) Complexes with Acetate Bridges. Crystal Structure of $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$[1,2]

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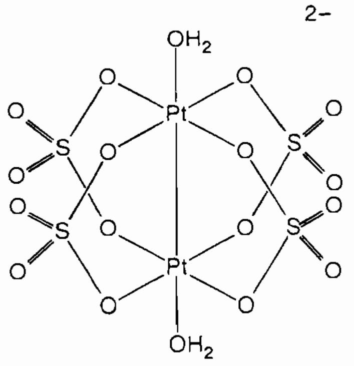
Reaction of $K_2[Pt(^{15}NO_2)_4]$ under argon with 1 M $HClO_4$ or CF_3SO_3H gave an initial blue solution ($\lambda_{max} = 627$ nm), due to nitrosyl complexes of platinum(IV). With heating, the color faded, and ^{195}Pt and ^{15}N NMR peaks were observed from *cis*-$[Pt(^{15}NO_2)_2(H_2O)_2]$, $[Pt(^{15}NO_2)(H_2O)_3]^+$, and *fac*-$[Pt(^{15}NO_2)_3(H_2O)_3]^+$. In air or oxygen, reaction was faster, giving $[Pt(H_2O)_4]^{2+}$ as well as mixed nitrito-*N*/aqua platinum(II) complexes, and larger proportions of platinum(IV) complexes, including $[Pt(OH)_6]^{2-}$ in solution, and solid $H_2[Pt(OH)_6]$. With 0.5 M H_2SO_4, reactions were similar, but a greater variety of platinum(IV) complexes were formed, some probably containing coordinated sulfate. With 1 M HNO_3, $K_2[Pt(NO_2)_6]$ formed. Reactions of $K_2[Pt(NO_2)_4]$ with aqueous acetic acid gave mixtures of Pt(II) and Pt(IV) mononuclear complexes and dinuclear Pt(III) complexes containing acetate bridges. The composition of the solution depended on the reaction conditions (heated for various times with argon, air, or oxygen above the solution or bubbled through). Crystals of $K_2[\{Pt^{II}(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$ were obtained from a reaction under argon, and the crystal structure was determined by X-ray diffraction: space group $P\bar{1}$ (no. 2); $a = 7.202(2)$ Å; $b = 8.987(2)$ Å; $c = 13.592(2)$ Å; $\alpha = 94.01(2)°$; $\beta = 90.68(2)°$; $\gamma = 111.04(2)°$; $Z = 2$; $R = 0.0371$, for 2875 reflections. The structure showed two acetate ligands bridging between *cis*-$Pt(NO_2)_2$ units, with the Pt−Pt distance 2.986(1) Å. Reactions of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ with various oxidants in the presence of acetic acid were studied. $[\{(CH_3CO_2)Pt^{III}(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ is formed by the oxidation of preformed $[\{Pt^{II}(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$. Under anaerobic conditions, the major oxidant is HNO_3 formed in the reaction mixture. Oxidation of $[\{Pt^{II}(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ with NO_2 formed in the reaction mixture in the presence of oxygen provides one route to $[(O_2N)Pt^{III}(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt^{III}(NO_2)_2(O_2CCH_3)]^{2-}$. Continued heating of solutions containing these Pt(III) complexes eventually gave solutions containing $[\{(CH_3CO_2)Pt^{III}(NO_2)\}_2(\mu\text{-}CH_3CO_2)_3]^-$.

Introduction

The platinum(III) dimeric anion, $[\{(H_2O)Pt(\mu\text{-}SO_4)_2\}_2]^{2-}$ (**2**),[3] is prepared by reaction of $K_2[Pt(NO_2)_4]$ (**1**) or *cis*-$[Pt(NO_2)_2(NH_3)_2]$ with 50% H_2SO_4 solution.[4,5] Analogous reactions with phosphoric acid give $[\{(H_2O)Pt(\mu\text{-}HPO_4)_2\}_2]^{2-}$ (**3**).[6,7] The mechanisms of these reactions have not been established. To provide some insight into the chemistry involved, we investigated the reactions of **1** with dilute aqueous solutions of strong mineral acids HA in which the anion A^- (perchlorate, ClO_4^-, or trifluoromethanesulfonate, $CF_3SO_3^-$) has a lower tendency to coordinate than sulfate or phosphate. We also studied the reactions of **1** with acetic acid, with the initial aim of preparing $[\{(H_2O)Pt(\mu\text{-}CH_3CO_2)_2\}_2]^{2+}$ (**4**). Although we were not able to prepare **4** by reaction of **1** with aqueous acetic acid alone, these reactions did produce in solution other Pt(III) complexes containing both nitrite and acetate. Our study of these reactions, described in this paper, provided some understanding of the major reaction pathways which lead to Pt(III)



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⊗ Abstract published in *Advance ACS Abstracts*, November 1, 1995.

(1) Part 1: Appleton, T. G.; Barnham, K. J.; Hall, J. R.; Mathieson, M. T. *Inorg. Chem.* **1991**, *30*, 2751.

(2) In accordance with the most recent IUPAC recommendation, "nitrito-*N*" will be used in the text for N-bound nitrite, but the older form "nitro" is retained in the title for consistency with other papers in this series.

(3) In formulas of symmetric dinuclear species, the following order of ligands is used consistently in this paper: [{axial ligand)(metal)(equatorial ligands)(μ-bridging ligands)}₂]ⁿ⁻. For unsymmetric dinuclear complexes, the order is: [(axial ligand)(metal 1)(equatorial ligands)(μ-bridging ligands)(metal 2)(equatorial ligands)(axial ligand)]ⁿ⁻.

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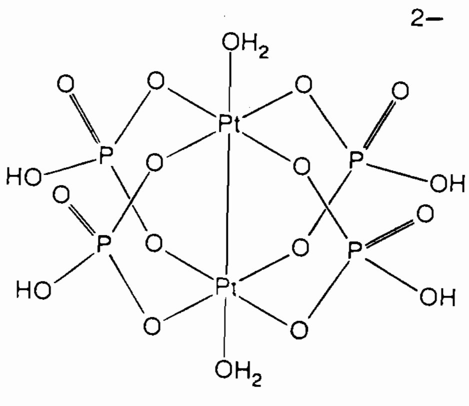

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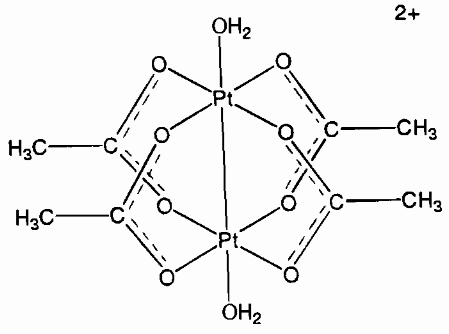
complexes, which, in turn, led us to a successful synthesis of **4**, published elsewhere.[8,9]



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In order to monitor reactions and characterize complexes in solution, we have used ^{195}Pt NMR, and, with high ^{15}N enrichment of the nitrite ligands in the starting material, **1**, ^{15}N NMR (^{195}Pt, $I = {}^1/_2$, 34% abundance; ^{15}N, $I = {}^1/_2$). The coupling pattern in ^{195}Pt NMR spectra allows immediate identification of the number of [^{15}N]nitrite ligands bound to a Pt atom, and, following our earlier work on NMR spectra of complexes $[Pt(^{15}NO_2)_3Z]^{m-}$,[1] δ_{Pt}, δ_N, and $^1J(^{195}Pt-^{15}N)$ can provide useful information about the oxidation state of the metal and about the ligands, other than nitrite, which are present in the complex.

Experimental Section

Starting Materials. Sodium nitrite highly enriched in ^{15}N (CIL) was supplied by Novachem (Melbourne, Australia). $K_2[Pt(NO_2)_4]\cdot 2H_2O$ (**1**) was prepared as previously described.[1] Solutions containing *cis*-$[Pt(NO_2)_2(H_2O)_2]$ or $[Pt(NO_2)_3(H_2O)]^-$ were prepared by reaction of **1** with sulfamic acid, as previously described.[1]

NMR Spectra. The 21.4-MHz ^{195}Pt ($I = {}^1/_2$, 33.6% abundance) and 10.1-MHz ^{15}N ($I = {}^1/_2$) NMR spectra were obtained with the use of a JEOL FX-100 instrument, as previously described.[1] The 42.9-MHz ^{195}Pt and 20.3-MHz ^{15}N NMR spectra were run without lock on a Bruker AC-200F instrument equipped with a 10-mm broad band tunable probe. For these ^{15}N spectra the magnetization tilt angle was 22°, the spectrum width was 20 kHz, and 500–10 000 pulses 5.7 s apart were used.

Shifts are positive to higher frequency. The reference for ^{15}N spectra was the $^{15}NH_4^+$ signal from a 5 M solution of $(^{15}NH_4)_2SO_4$ in 1 M H_2SO_4 in a coaxial capillary. The reference for ^{195}Pt spectra was a separate sample of $Na_2[PtCl_6]$ (0.5 g in 2 mL). All spectra were run without ^{1}H decoupling.

Because of the effect of chemical shift anisotropy-induced relaxation, "satellite" peaks from coupling to ^{195}Pt were relatively broad in 20.3-MHz ^{15}N spectra of platinum(II) complexes. The $^{195}Pt-^{15}N$ coupling constants were therefore measured, where possible, from 10.1-MHz ^{15}N spectra. On the other hand, there was much greater sensitivity in ^{15}N spectra run at higher field, and the ^{15}N shifts reported are those measured from 20.3-MHz spectra.

Reactions of 1 with Aqueous Solutions of Strong Acids. Aqueous acid (5–10 mL, 1 M H^+) was added to $K_2[Pt(^{15}NO_2)_4]\cdot 2H_2O$ (0.25 g) in a 25-mL round-bottomed flask immersed in an oil bath maintained at 80–90 °C. When desired, a gas (argon, air, or oxygen) was gently bubbled through the solution. For prolonged reaction times, small quantities of water were added periodically to maintain solution volume. Removal of the flask from the oil bath effectively quenched all reaction, and 2-mL aliquots could be transferred when desired to 10-mm NMR tubes to allow NMR spectra to be obtained. These samples could then be returned to the reaction flask and the reaction resumed. *CAUTION!* The reactions of $K_2[Pt(NO_2)_4]$ with acids generate toxic oxides of nitrogen and should be carried out in a hood.

Reactions of 1 with Aqueous Acetic Acid. For reactions carried out under argon, $K_2[Pt(NO_2)_4]\cdot 2H_2O$ (0.2 g) and 4 mL of a glacial acetic acid/water mixture (3:1 by volume) were placed in a Schlenk tube. The tube was evacuated by a freeze–thaw process and then flushed with argon. This process was repeated four or five times, to ensure that all of the air was removed. A slow, steady stream of argon was then bubbled through or passed over the solution, which was heated, with stirring, by immersion in an oil bath maintained at a temperature between 70 and 105 °C. For reactions carried out under oxygen or air, the preliminary evacuation was omitted.

Preparation of $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$. The following preparation was repeated several times, with the nitrite ligands being either ^{14}N or ^{15}N. Yields were variable, up to 25%, depending on the extent to which acetic acid and water were removed by evaporation during the reaction. A solution of $K_2[Pt(NO_2)_4]$ in a 3:1 acetic acid/water mixture was heated under an argon atmosphere, as described above, for 40–60 min at 90 °C, and then allowed to cool slowly, still under argon. Bright yellow platelike crystals deposited. The mother liquor was removed by pipet, and the crystals were washed with a small volume of the acetic acid/water mixture and then dried in a stream of argon. Anal. Calcd for $C_4H_8K_2N_4O_{13}Pt_2$: C, 6.1; H, 1.0; N, 7.1. Found: C, 6.1; H, 1.1; N, 7.0.

Determination of Crystal Structure of $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$. A thin plate-shaped yellow crystal (approx. 0.25 × 0.24 × 0.08 mm) was used for data collection using graphite-monochromatized Mo Kα radiation. Unit cell dimensions were obtained by least-squares refinement using 25 centered reflections for which $30° < 2\theta < 34°$. Intensity data were taken on an Enraf-Nonius CAD4 four-circle diffractometer. Three standard reflections, monitored every 100 reflections, showed no significant loss of intensity during data collection. Data reduction (SDP package), including corrections for Lorentz and polarization effects and empirical absorption correction,[10] gave 2876 unique reflections in the range $3° < 2\theta < 50°$. The platinum positions were determined from a Patterson synthesis (SHELXS),[11] and the remaining non-hydrogen atoms were located by difference syntheses (SHELXL).[12] Atom positional and anisotropic thermal parameters were refined using full-matrix least squares. One reflection (0,0,2) was considered to be suffering from extinction and was removed before the final cycle. Hydrogen positions could not be located on the difference maps, so they were generated. Aspects of the data collection, and crystallographic parameters, are summarized in Table 1.

Reaction of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ with $CH_3CO_2H/H_2O/HNO_3$ under Argon. A solution of *cis*-$[Pt(NO_2)_2(H_2O)_2]$, prepared by reaction of 0.5 g $K_2[Pt(NO_2)_4]\cdot 2H_2O$ (**1**) (1.1 mmol) with sulfamic acid in 2 mL of water,[1] was placed in a Schlenk tube having a septum on one outlet. Glacial acetic acid (6 mL) was added. The tube was repeatedly

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Table 1. Crystallographic Data for $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$[a]

empirical formula	$C_4H_8K_2N_4O_{13}Pt_2$	Z	2
fw	788.52	T, K	293
space group	$P\bar{1}$	λ, Å	0.71073 (Mo Kα)
a, Å	7.202(2)		
b, Å	8.987(2)	ρ(calcd), g cm^{-3}	3.199
c, Å	13.592(2)	μ, cm^{-1}	176.57
α, deg	94.01(2)	$T_{\min}$	0.17
β, deg	90.68(2)	$T_{\max}$	0.90
γ, deg	111.04(2)	R	0.0371
V, Å^3	818.4(3)	R_w	0.1226

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = \{(\Sigma[\omega(F_o^2 - F_c^2)]^2)/\Sigma[\omega F_o]^2\}^{1/2}$.

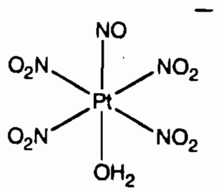
evacuated and flushed with argon, using a freeze−thaw technique. Heating in an oil bath at 90 °C was then commenced, with argon either by gentle bubbling through the solution or as an atmosphere in the tube. Argon was bubbled briefly through liquids to be introduced through the septum. At each of the times 2, 20, and 40 min after heating commenced, 1 mol equiv (with respect to platinum) portions of 1 M HNO_3 (*i.e.*, 1.1-mL aliquots) were added. Acetic acid was also added from time to time to maintain the CH_3CO_2H/H_2O ratio close to 3:1. Periodically, the reaction vessel was allowed to cool to quench the reaction, and 2-mL aliquots of the reaction mixture were removed from the tube for NMR examination.

A similar procedure was carried out using freshly-prepared HNO_2 solution rather than HNO_3. Each nitrous acid aliquot was prepared by addition of 1.1 mL of ice-cold degassed 1 M $HClO_4$ solution to 0.075 g of solid sodium nitrite under argon.

Reaction of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ with CH_3CO_2H/H_2O and NO_2. An aqueous solution of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ was prepared from 0.5 g (1.1 mmol) of $K_2[Pt(NO_2)_4]\cdot 2H_2O$, acetic acid was added, and the solution was degassed, as described above. Once heating under argon was commenced, nitrogen dioxide (3 mol equiv/(mol of Pt)) was slowly carried into the reaction mixture in a stream of argon. NO_2 (with either ^{14}N or ^{15}N) was prepared by addition of 20% sulfuric acid to a solution of 0.35 g of $NaNO_2$ in 1 mL of water, in air.[13] The NO_2 was then condensed into a Schlenk tube at −15 °C and excess air pumped away. A slow stream of argon was passed through the Schlenk tube as it was allowed to warm and bubbled through the reaction mixture. *CAUTION!* Nitrogen dioxide is a poisonous gas.

Results

Reactions of $K_2[Pt(^{15}NO_2)_4]$ (1) with $HClO_4$ and CF_3SO_3H Solutions (Scheme 1). Reactions with 1 M solutions of these two acids gave similar results. At ambient temperature in air, a faint blue color was observed within a few minutes. If the solution was then heated at 80−90 °C, the blue color intensified and a brown gas (NO_2) was liberated. If the solution was cooled to 25 °C, the blue color persisted indefinitely. The visible absorption spectrum of the solution showed a peak with λ_{max} = 627 nm. EPR spectra of a frozen $HClO_4$ solution at 78 K showed no signals. NMR spectra of such solutions showed relatively weak, broad peaks, presumably because of the effect of the paramagnetic blue species. Dinitrogen trioxide, N_2O_3, is blue, but the color could not be due to this species, which is too unstable to persist at the temperatures used[14] and would be blown from the solution by passage of a stream of gas. Compounds containing platinum in mixed II/III oxidation states can also be colored, such as the "blues" formed with diammineplatinum and α-pyridonate[15] or phosphate.[16] These compounds have ligands bridging between Pt atoms. Because perchlorate and trifluoromethanesulfonate are very poor ligands for platinum(II),[17] such bridges would not be expected to form here. The blue color of these solutions may therefore confidently be ascribed to nitrosylplatinum(IV) complexes. Peterson *et al.*[18] isolated the deep blue nitrosyl complex $K[Pt(NO_2)_4(NO)(H_2O)]$ (**5**) from the reaction of **1** with 3:1 H_3PO_4/H_2O



5

under argon and determined its structure by X-ray diffraction. After addition of chloride, green $K_2[PtCl_3(NO_2)_2(NO)]$ was isolated, and its crystal structure was also determined.[18] These compounds are thought to contain Pt(IV) bound by NO^-. Reaction of $(NO)(BF_4)$ with an aqueous solution of **1** also gave a blue solution (λ_{max} = 625 nm).

When heating of the solution in air was continued, the blue color faded, with the solution turning green (blue + yellow), then straw yellow. The ^{15}N and ^{195}Pt NMR spectra of a solution (with ^{15}N-labeled nitrite) heated long enough for the green color to have just disappeared showed several sets of peaks. First, there was a strong, sharp singlet in the ^{15}N spectrum at 353.4 ppm from $^{15}NO_3^-$. The strongest peaks from platinum complexes were a 1:2:1 triplet in the ^{195}Pt NMR spectrum at −1365 ppm, and a singlet with satellites in the ^{15}N spectrum (374.6 ppm, J(Pt−N) = 790 Hz), which corresponded to *cis*-$[Pt(^{15}NO_2)_2(H_2O)_2]$ (**7**) (Scheme 1) (previously prepared in solution from reaction of **1** with 2 mol of sulfamic acid[1]). Relatively weak peaks were also present from $[Pt(^{15}NO_2)_3(H_2O)]^-$ (**6**) (also previously prepared:[1] ^{195}Pt spectrum, doublet of triplets at −1797 ppm; ^{15}N spectrum two singlets with satellites, intensity ratio 2:1, δ_N 407.8, J(Pt−N) = 572 Hz for mutually trans nitrite ligands, and δ_N 382.1, J(Pt−N) = 821 Hz for nitrite trans to H_2O). With further heating, the peaks due to the trinitrito complex **6** slowly disappeared, while peaks grew that could be assigned to $[Pt(^{15}NO_2)(H_2O)_3]^+$ (**8**) (^{195}Pt spectrum, doublet at −829 ppm; ^{15}N spectrum singlet at 360.9 ppm, with satellites, ^1J(Pt−N) = 716 Hz) and $[Pt(H_2O)_4]^{2+}$ (**9**) (^{195}Pt spectrum, singlet at +42 ppm[19,20]).

The NMR spectra also showed peaks due to Pt(IV) complexes. After the solution was heated for 30 min, the ^{195}Pt spectrum showed two singlets, at +3370 ppm and at +3040 ppm. The lack of any splitting from coupling with ^{15}N showed that these peaks were due to complexes which did not contain any N-coordinated nitrite. The peak at 3370 ppm corresponded to $[Pt(OH)_6]^{2-}$ (**10**).[21] The assignment of the peak at 3040 ppm was uncertain. It was not likely to be due to a species with perchlorate or triflate bound, but perhaps nitrate, which was certainly present at this stage (see above), was coordinated, in a complex such as $[Pt(OH)_5(ONO_2)]^{2-}$. The ^{195}Pt NMR spectra

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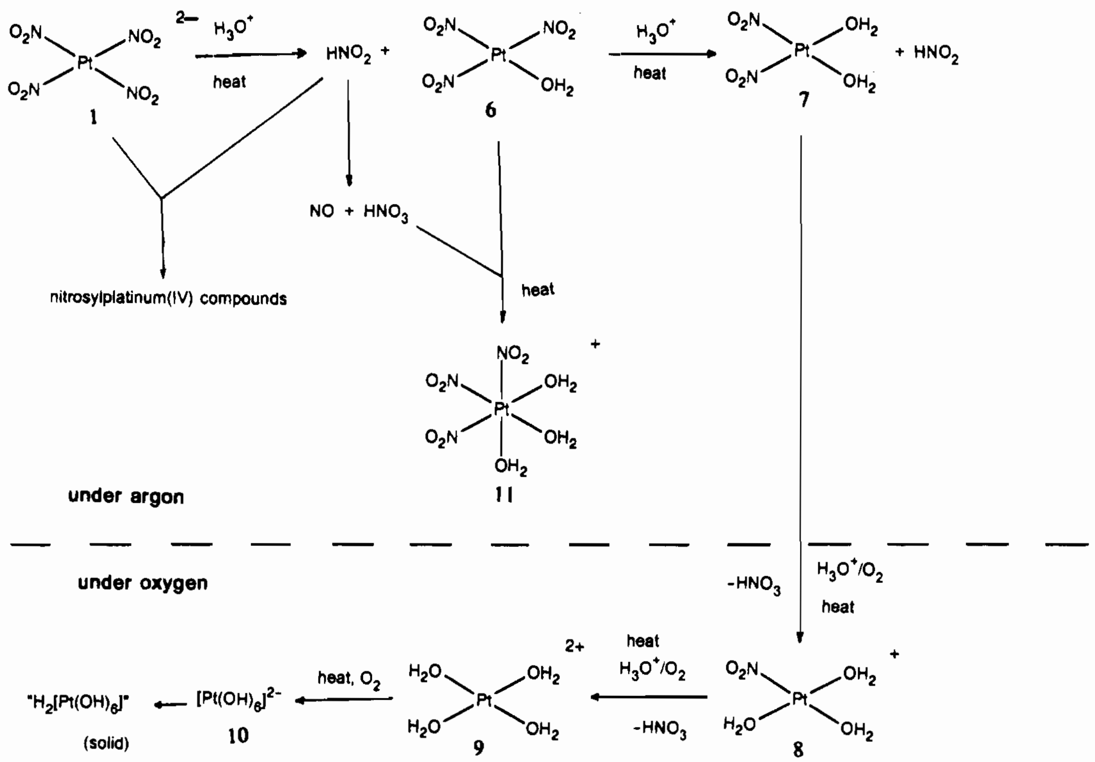
Scheme 1



of these solutions (obtained with ^{15}N-enriched nitrite) also showed a number of peaks near 2370 ppm. The major peaks were a 1:3:3:1 quartet with splitting of 550 Hz. The corresponding peak in the ^{15}N spectrum was a singlet with satellites (sharp even at 20.3 MHz for this octahedral complex) at 321.3 ppm (J(Pt−N) = 551 Hz). This relatively high Pt^{IV}−N coupling constant must correspond to nitrite trans to an O-donor ligand, such as water.[22] These peaks were therefore assigned to *fac*-$[Pt(^{15}NO_2)_3(H_2O)_3]^+$ (**11**). The peaks overlapping with those from **11** in the ^{195}Pt NMR spectrum and a peak at 318.8 ppm in the ^{15}N NMR spectrum were probably due to *fac*-trinitrito-*N* complexes with one or more nitrate ions bound in place of water.

If the solution from **1** with triflic or perchloric acid was heated in air for more than 50 min, copious amounts of an orange solid precipitated, whose properties corresponded to "$H_2[Pt(OH)_6]$".[23,24] If the reactions of **1** with these acids were carried out under oxygen, rather than air, the reactions proceeded much more quickly. Blue and green colors were observed for only 3−5 min before fading. The NMR spectra of the resultant solutions were similar to those described above. After only 15−20 min, much $H_2[Pt(OH)_6]$ had precipitated.

If the reaction was carried out under argon (either under an argon atmosphere or with argon blowing through the solution), the reactions occurred more slowly than under air or oxygen. The blue color persisted for 20 min at 80−90 °C, followed by 20−25 min when the solution was green. The NMR spectra of the yellow solution obtained after 45 min showed peaks from $^{15}NO_3^-$, *cis*-$[Pt(^{15}NO_2)_2(H_2O)_2]$ (**7**), $[Pt(^{15}NO_2)(H_2O)_3]^+$ (**8**), and *fac*-$[Pt(^{15}NO_2)_3(H_2O)_3]^+$ (**11**). Continued heating, up to 5 h, caused little further change. In contrast to the reaction in air, no solid precipitated.

The reaction of coordinated nitrite with aqueous acid, eq 1, would produce nitrous acid, from which NO^+ is formed in strong acid (eq 2).[25]

$$Pt-(NO_2^-) + H_3O^+ \rightarrow Pt-OH_2 + HNO_2 \qquad (1)$$

$$HNO_2 + H_3O^+ \rightleftharpoons NO^+ + 2H_2O \qquad (2)$$

Reaction of NO^+ with $[Pt(NO_2)_4]^{2-}$ (**1**) would give blue $[Pt(NO_2)_4(NO)(H_2O)]^-$ (**5**), and similar reactions with other platinum(II) complexes could form other platinum(IV) nitrosyl complexes. Nitrite bound to some metals (*e.g.*, iron in $[Fe(CN)_5(NO_2)]^{4-}$) reacts reversibly with more dilute acids than free nitrous acid, to give complexes containing bound NO^+ (*e.g.*, $[Fe(CN)_5(NO)]^{2-}$).[25−28] A complex such as **5**, with four intact nitrite ligands in addition to nitrosyl, would be unlikely to be formed *via* such intermediates, and additional oxidants would be required to produce any platinum(IV) nitrosyl complexes by this route. The replacement of nitrite coordinated to Pt(II) by water did proceed much more rapidly when dioxygen was present. There could be a direct oxidation of bound nitrite (eq 3) or, possibly, oxidation of an intermediate NO^+ complex (eq 4).

$$Pt-(NO_2^-) + {}^1/_2O_2 \rightarrow Pt-(NO_3^-) \qquad (3)$$

$$Pt-(NO^+) + H_2O + {}^1/_2O_2 \rightarrow Pt-(NO_3^-) + 2H^+ \qquad (4)$$

The oxygen-assisted reaction would become increasingly important in removing the remaining nitrite ligands from mono- and bis(nitrito-*N*) complexes **8** and **7**. In the reactions of **1** with sulfamic acid, the first and second nitrite ligands were more

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[28] We thank a reviewer for suggesting that this reaction may be relevant to our systems

easily removed than the remaining coordinated nitrite ligands.[1] In a similar way, in the reactions of **1** with strong acids, the nitrite ligands were progressively more difficult to remove. This is probably due primarily to the lower trans effect of water (trans to nitrite in **7** and **8**) compared with nitrite, although the effect of the increasing overall positive charge on the complex may also be significant. Thus, removal of all coordinated nitrite ligands from **1** to give $[Pt(H_2O)_4]^{2+}$ (**9**) did not occur significantly in the absence of oxygen. We had originally hoped that these reactions under argon might provide an alternative to the existing preparation of solutions of $[Pt(H_2O)_4]^{2+}$, which is time-consuming,[29] but the dioxygen needed to remove all coordinated nitrite from Pt(II) also caused the formation of large amounts of platinum(IV) compounds.

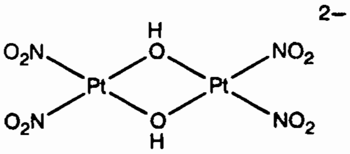
The nitrous acid formed from reaction 1 would produce nitric acid and nitric oxide (eq 5), and, in the presence of oxygen, nitrogen dioxide would be formed (eq 6).

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \qquad (5)$$

$$NO + {}^1/_2O_2 \rightarrow NO_2 \qquad (6)$$

Even in the complete absence of oxygen, significant amounts of the platinum(IV) complex, **11**, were formed, probably by oxidation of platinum(II) complexes by nitric acid formed from reactions 1 and 5 (see Discussion below on the role of nitric acid oxidation in acetic acid systems). When oxygen was present, platinum(IV) products were formed in much greater quantities. The major route then was probably by direct reaction of platinum(II) precursors with O_2. Nitric acid would also be present in higher concentrations (from more efficient cleavage of Pt(II)−NO_2 groups and from reaction of NO_2, generated from reaction 6, with solvent water).

Reactions of 1 with Sulfuric Acid. When a solution of $K_2[Pt(^{15}NO_2)_4]$ (**1**) was heated with 0.5 M H_2SO_4 in air, the blue/green/yellow color sequence was complete within 15 min at 80−90 °C. The ^{15}N NMR spectrum of the resultant solution showed peaks due to *cis*-$[Pt(^{15}NO_2)_2(H_2O)_2]$ (**7**), $[Pt(^{15}NO_2)_3(H_2O)]^-$ (**6**), and a small amount of unreacted **1**. Min *et al.*[30] isolated $K_2[\{Pt(NO_2)_2(\mu\text{-}OH)\}_2]\cdot 1.5H_2O$, containing the anion **12**, from reaction of **1** with dilute H_2SO_4, followed by neutralization of excess acid with K_2CO_3. We have shown[1] that **12** and the trinuclear analogue, **13**, form readily when alkali is added to a solution of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**). The 21.4-MHz ^{195}Pt NMR spectrum of our reaction mixture showed a 1:3:3:1 quartet at +2660 ppm, with a line separation of 550 Hz. This pattern was again assigned to *fac*-$[Pt(^{15}NO_2)_3(H_2O)_3]^+$ (**11**), with a significant "solvent effect" accounting for the difference in chemical shift from that in triflic acid. It was likely that these peaks (line width = 25 Hz) overlapped with those from a sulfato complex (*e.g.*, $[Pt(^{15}NO_2)_3(OSO_3)(H_2O)_2]^-$) as the ^{15}N NMR spectrum showed a number of singlets with satellites with Pt−N coupling constants near 550 Hz. Two peaks (322.2 ppm, *J*(Pt−N) = 550.5 Hz; 321.2 ppm, *J*(Pt−N) = 564.0 Hz) continued to grow with further heating.



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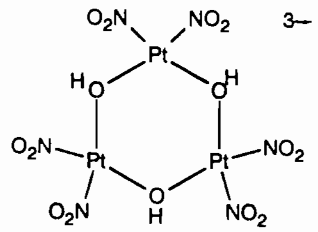
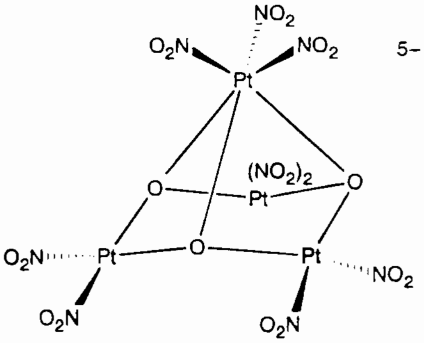


13

Previous workers have shown that simple platinum(IV) complexes form in the reactions of **1** with H_2SO_4. Evans and Fanwick[31] heated **1** with 50% sulfuric acid for 3−4 h and then passed the solution down an anion exchange column in the chloride form. They isolated *cis*-$K_2[PtCl_4(NO_2)_2]$ and determined its crystal structure. Min *et al.*[30] isolated $K_5[\{fac\text{-}Pt^{IV}(NO_2)_3\}(\{Pt^{II}(NO_2)_2(\mu\text{-}O)\}_3)]$ (**14**) from the neutralized solution from reaction of **1** with dilute H_2SO_4 and determined its structure. The structure was also independently determined by Koz'min *et al.*[32] This compound is an adduct between *fac*-$Pt^{IV}(NO_2)_3$ and an oxo-bridged trimer, formed by deprotonation of **13**. Formation of **14** would have occurred when alkali was added to a solution containing both *fac*-$[Pt(NO_2)_3(H_2O)_3]^+$ (**11**) and *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**).



14

Although reaction of **1** with H_2SO_4 is the preparative route to the platinum(III) sulfate, **2**, our ^{195}Pt NMR spectra showed neither the characteristic singlet from **2** at +1756 ppm[7] nor any peaks assignable to other platinum(III) species. This is probably due to the low sulfuric acid concentration in our reaction (0.5 M) compared with that in the preparative reaction (50%). A higher sulfate concentration would greatly increase the proportion of mixed sulfato/nitrito-*N* complexes of platinum(II) in the early stages of the reaction, including dinuclear complexes with bridging sulfate. As outlined in the Discussion below, it is the oxidation of these dinuclear complexes that provides the major pathway to platinum(III) complexes.

Reaction of 1 with Nitric Acid. When a solution of **1** in 1 M HNO_3 was heated, blue and then green solutions were obtained, with the precipitation of a yellow solid, which was identified from its IR spectrum as $K_2[Pt(NO_2)_6]$.[33,34] The

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Scheme 2

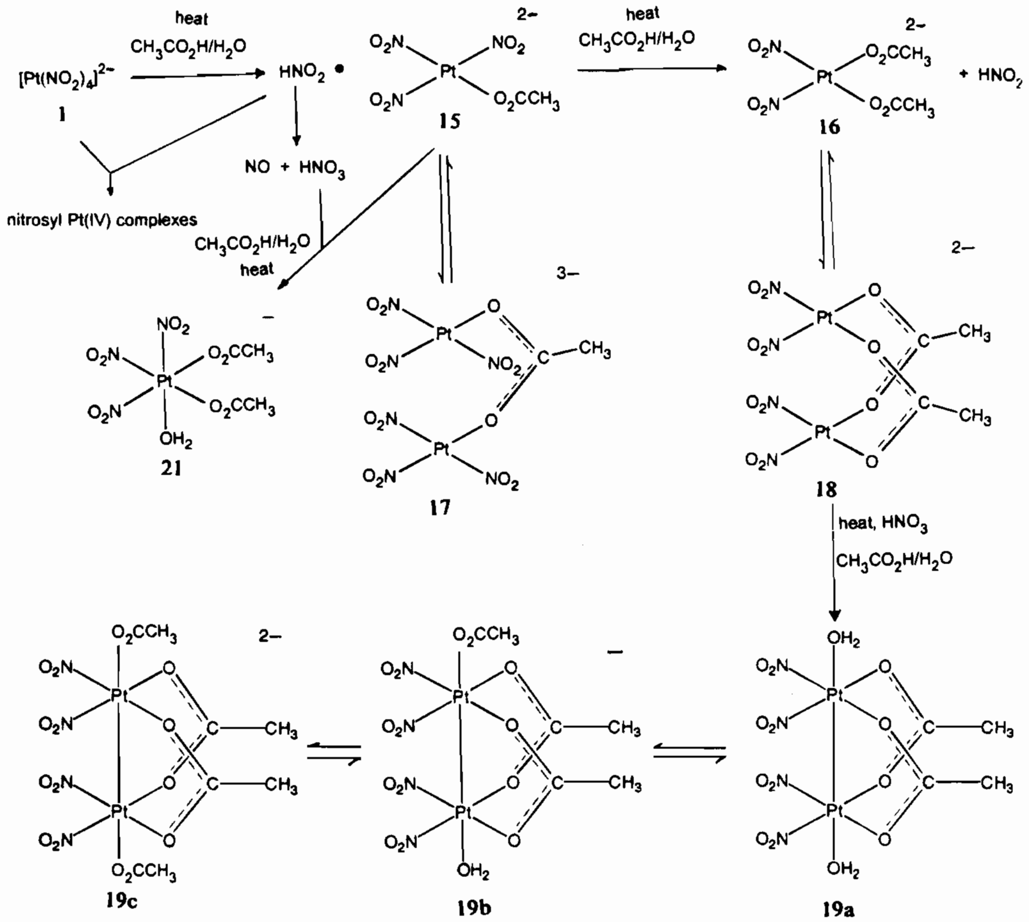

Table 2. Isotopomers of Platinum(III) Dimer

	abundance		abundance
i X–Pt$_{(1)}$–Pt$_{(2)}$–Y	$^4/_9$	iii X–Pt$_{(1)}$–*Pt$_{(2)}$–Y	$^2/_9$
ii X–*Pt$_{(1)}$–Pt$_{(2)}$–Y	$^2/_9$	iv X–*Pt$_{(1)}$–*Pt$_{(2)}$–Y	$^1/_9$

[a] An asterisk indicates ^{195}Pt (abundance taken as $^1/_3$).

standard preparation of this compound is by reaction of **1** with HNO_3, with NO_2 passed through the solution.[33,34]

Reaction of $[\{(H_2O)Pt(\mu\text{-}SO_4)_2\}_2]^{2-}$ with Acetic Acid. Preliminary to the study of reactions of **1** with aqueous acetic acid, it was desirable to determine the effect generally on ^{195}Pt NMR spectra of replacing axial water ligands by acetate. The effect of axial ligand substitution on ^{195}Pt NMR spectra of sulfate-bridged Pt(III) complexes $[XPt(\mu\text{-}SO_4)_4PtY]^{n-}$ has been well-examined, but acetate was not among the ligands studied previously.[7] A solution of $Na_2[\{(H_2O)Pt(\mu\text{-}SO_4)_2\}_2]$ (**2**) in water shows a single ^{195}Pt NMR peak at 1756 ppm. Sodium acetate (10 mol equiv) was added to an aqueous solution of **2**. The ^{195}Pt spectrum now showed a sharp peak at 1929 ppm, assigned to $[\{(CH_3CO_2)Pt(\mu\text{-}SO_4)_2\}_2]^{4-}$. In a separate experiment, $Na_2[\{(H_2O)Pt(\mu\text{-}SO_4)_2\}_2]$ was dissolved in 3:1 (by volume) acetic acid/water mixture, and 2 mol equivalents (relative to **2**) of sodium acetate was added. The ^{195}Pt NMR spectrum showed three peaks of similar intensity, at 2126, 1952, and 1590 ppm. The peak at 1952 ppm was assigned to $[\{(CH_3CO_2)Pt(\mu\text{-}SO_4)_2\}_2]^{4-}$, with the shift from that in water due to a solvent effect. The remaining peaks were assigned to the unsymmetrical complex $[(CH_3CO_2)Pt(\mu\text{-}SO_4)_4Pt(H_2O)]^{3-}$. The isotopomers of a dinuclear platinum(III) complex are shown in Table 2. Isotopomer i, with no ^{195}Pt, will, of course, give no peak in the ^{195}Pt NMR spectrum. In this unsymmetrical complex, isotopomers ii and iii are different. Each would give a single peak. The peak at 2126 ppm was probably due to platinum bound by acetate, and that at 1590 ppm, to platinum bound by water. Isotopomer iv, with two ^{195}Pt nuclei, would be expected to give an AB pattern, but this was too weak to be observed.

If these observations on sulfate-bridged complexes may be extrapolated to dinuclear platinum(III) compounds in general, it would be expected that replacement of axial water by axial acetate will cause deshielding of the platinum nucleus, that there will be a large chemical shift difference between the Pt atoms bound to acetate and water in an unsymmetrical acetato/aqua complex, and that δ_{Pt} may be affected significantly if the composition of mixed acetic acid/water solvents is changed.

Reactions of 1 with Aqueous Acetic Acid under Argon (Scheme 2). When the initially colorless solution of $K_2[Pt(^{15}NO_2)_4]$ (**1**) was heated at 90 °C under argon with a 3:1 (by volume) acetic acid/water mixture, the solution initially turned green (5–20 min after commencement). The visible absorption spectrum showed a peak with $\lambda_{max} = 627$ nm. As with blue or green solutions in the other systems discussed above, NMR spectra showed only weak, broad peaks. After 20 min, the solution became yellow. The color then slowly deepened through orange (40 min) to brown (60 min). The ^{195}Pt NMR spectrum of the yellow solution after 20 min of heating showed only peaks due to platinum(II) species. The most intense peaks were a doublet of triplets at −1832 ppm (doublet separation of 734 Hz, triplet separation of 576 Hz) and a 1:2:1 triplet at −1447 ppm (J(Pt–N) = 730 Hz). From our previous study,[1] these signals could be assigned respectively to $[Pt(^{15}NO_2)_3(-O_2CCH_3)]^{2-}$ (**15**) and to *cis*-$[Pt(^{15}NO_2)_2(-O_2CCH_3)_2]^{2-}$ (**16**) (Scheme 2). There was also a very weak doublet of triplets at −1949 ppm (doublet splitting of 748 Hz, triplet splitting of 535 Hz) which we have previously assigned[1] to a complex with a

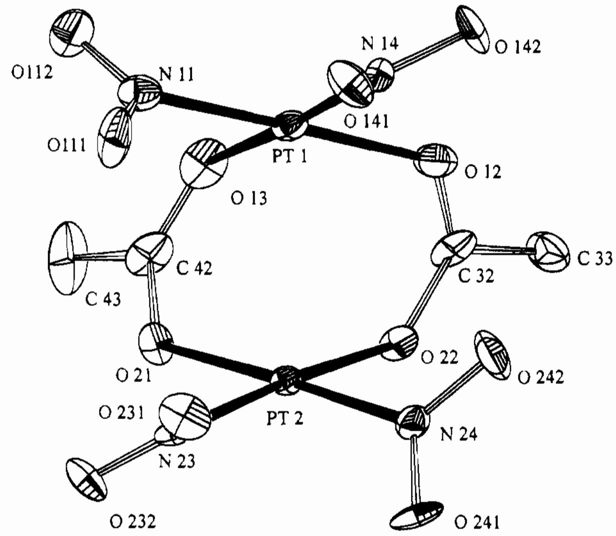

Figure 1. ORTEP diagram (PLATON) with 30% probability ellipsoids showing the structure of the anion in $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$. Hydrogen atoms are omitted.

bridging acetate, $[\{Pt(^{15}NO_2)_3\}_2(\mu\text{-}O_2CCH_3)]^{3-}$ (**17**). A remaining very weak 1:2:1 triplet at −1572 ppm (J(Pt−N) = 678 Hz) was assigned to $[\{Pt(^{15}NO_2)_2(\mu\text{-}O_2CCH_3)\}_2]^{2-}$ (**18**). The significantly increased nuclear shielding in the two complexes where the Pt atoms are brought into close proximity by the bridging acetate may be compared with analogous shifts in complexes with α-pyridonate bridges.[35,36]

The ^{195}Pt NMR spectrum of the orange solution obtained after 40 min showed that the dominant complex present was *cis*-$[Pt(^{15}NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**), together with small amounts of the complex with acetate bridges, **18**, and the tri(nitrito-*N*)platinum(II) complex, **15**. The spectrum also showed weak peaks (approximately 10% of the total intensity) from platinum(III) complexes, **19a** and **19c**. Since these peaks became much stronger after further heating, they will be discussed later.

When such a solution (prepared from **1** with either ^{14}N or ^{15}N present) was allowed to stand, bright yellow platelike crystals deposited. The IR spectrum of the solid showed strong peaks from water of crystallization (3447 and 1617 cm^{-1}), nitrite (1396, 1328, 847, and 840 cm^{-1}), and acetate (1560 and 1437 (shoulder) cm^{-1}). Microanalysis was consistent with the empirical formula $KPt(NO_2)_2(CH_3CO_2)\cdot 0.5H_2O$. The crystal structure determination by X-ray diffraction showed that the compound was $K_2[\{Pt(NO_2)_2(\mu\text{-}O_2CCH_3)\}_2]\cdot H_2O$, the potassium salt of the anion **18**. The structure of the anion is illustrated in Figure 1. Crystallographic parameters are listed in Table 1, and positional parameters are given in Table 3. Selected bond lengths and angles are listed in Table 4. Each Pt atom has approximate square planar coordination. The two PtN_2O_2 planes are tilted at an angle of 39.5(1)°. The Pt−Pt distance, 2.986(1) Å, is comparable to those in other compounds in which two Pt^{II} atoms are bridged by two cis three-atom bridges (*e.g.*, $[\{Pt(NH_3)_2(\mu\text{-}\alpha\text{-pyridonate})\}_2]^{2+}$, 2.90 Å;[35] $[\{Pt(NH_3)_2(\mu\text{-}1\text{-methylthyminate})\}_2]^{2+}$, 2.915(1) Å;[36] $[\{Pt(NH_3)_2(\mu\text{-}1\text{-methyluracilate})\}_2]^{2+}$, 2.937(1) Å;[37] $[\{Pt(NH_3)_2(\mu\text{-}1\text{-methylcytosinate})\}_2]^{2+}$, 2.981(2) Å [38]). In platinum(II) complexes of this kind, no formal metal−metal bond would be expected. However, there is some indication of an attractive force between the metal atoms in that each Pt atom is significantly out of its N_2O_2 coordination plane, toward the other Pt atom (Pt(1), 0.058(1) Å; Pt(2), 0.082(1) Å).[39] The increased shielding of the ^{195}Pt nuclei in the bridged dinuclear complexes (noted above) is probably due to interaction between the metal atoms. It is generally accepted that a Pt atom may be perturbed by another Pt atom in solids with a significantly greater Pt−Pt distance than 3.0 Å (*e.g.*, Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, where the Pt−Pt distance is 3.25 Å [40]). There are no close approaches of other atoms in the crystal lattice to the Pt atoms in the dinuclear anions.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $K_2[\{Pt(NO_2)_2\{\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$

	x	y	z	U(eq)[a]
Pt(1)	8199(1)	7181(1)	8082(1)	28(1)
Pt(2)	5156(1)	7951(1)	6924(1)	22(1)
K(1)	4296(6)	2020(4)	6915(3)	43(1)
K(2)	53(5)	2770(4)	5014(3)	34(1)
N(11)	10711(22)	8840(17)	7663(11)	36(3)
N(14)	8686(20)	5404(14)	7355(11)	31(3)
N(23)	6469(18)	9226(16)	5853(9)	24(3)
N(24)	3919(20)	6043(14)	6010(11)	30(3)
O(12)	5620(19)	5610(15)	8577(10)	42(3)
O(13)	7708(20)	8913(16)	8987(9)	43(3)
O(21)	6287(19)	9939(12)	7895(8)	33(3)
O(22)	3561(16)	6741(13)	8027(8)	31(2)
C(32)	4025(25)	5783(22)	8556(11)	35(4)
C(33)	2405(29)	4794(23)	9168(16)	46(5)
C(42)	7099(30)	9946(25)	8693(12)	43(4)
C(43)	7232(44)	11399(23)	9456(15)	69(8)
O(111)	11045(22)	9004(16)	6781(10)	54(4)
O(112)	11874(22)	9730(17)	8272(10)	51(4)
O(141)	9551(22)	5486(15)	6568(10)	47(3)
O(142)	8091(23)	4098(15)	7727(14)	65(5)
O(231)	7228(21)	8701(16)	5164(10)	46(3)
O(232)	6632(19)	10645(13)	5885(9)	37(3)
O(241)	3066(18)	6099(16)	5227(9)	44(3)
O(242)	3943(25)	4751(14)	6242(12)	59(4)
O(91)	9477(21)	7722(16)	2940(11)	52(3)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$

Pt(1)−N(14)	1.96(1)	Pt(1)−N(11)	2.01(2)
Pt(2)−N(23)	1.95(1)	Pt(2)−N(24)	1.96(1)
Pt(1)−O(12)	2.04(1)	Pt(1)−O(13)	2.05(1)
Pt(2)−O(22)	2.03(1)	Pt(2)−O(21)	2.05(1)
C(32)−O(12)	1.21(2)	C(32)−O(22)	1.29(2)
C(42)−O(13)	1.25(2)	C(42)−O(21)	1.23(2)
Pt(1)−Pt(2)	2.986(1)		
N(14)−Pt(1)−N(11)	94.0(6)	N(23)−Pt(2)−N(24)	91.9(6)
N(14)−Pt(1)−O(12)	89.9(6)	N(11)−Pt(1)−O(13)	89.1(6)
N(24)−Pt(2)−O(22)	89.2(5)	N(23)−Pt(2)−O(21)	89.6(5)
O(12)−Pt(1)−O(13)	86.9(5)	O(22)−Pt(2)−O(21)	89.0(4)
Pt(1)−O(12)−C(32)	124.8(12)	Pt(1)−O(13)−C(42)	124.3(11)
Pt(2)−O(21)−C(42)	123.5(12)	Pt(2)−O(22)−C(32)	126.5(10)
O(12)−C(32)−O(22)	126(2)	O(13)−C(42)−O(21)	128(2)

Each potassium ion interacts with 8 O-atoms, with K−O distances between 2.76 and 3.11 Å (K(1) with six O-atoms from nitrite groups, one from acetate, and one from water of crystallizaton; K(2) with seven O-atoms from nitrite groups and one from water of crystallization).

When the solid (containing [^{15}N]nitrite) was dissolved in water, the ^{15}N NMR spectrum run as soon as possible (at least 30-in accumulation) showed peaks due to an equilibrium mixture of *cis*-$[Pt(^{15}NO_2)_2(O_2CCH_3)(H_2O)]^-$ (**20**) (previously character-

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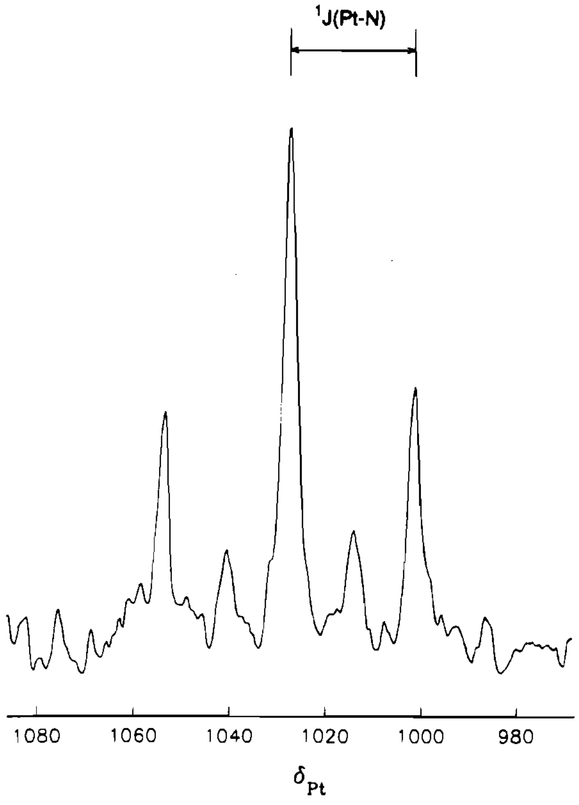

Figure 2. 42.8-MHz ^{195}Pt NMR spectrum of $[\{(CH_3CO_2)Pt(^{15}NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**19c**) obtained by heating $K_2[Pt(^{15}NO_2)_4]$ with 3:1 acetic acid/water under argon.

ized by ^{15}N and ^{195}Pt NMR[1]), *cis*-$[Pt(NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**), and *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**). In D_2O, 400-MHz ^{1}H NMR spectra could be run within 2−3 min, but the spectrum showed only singlets from the monomeric species **20** (1.98 ppm) and **16** (1.97 ppm) as well as free acetate (2.06 ppm). Spectra run in other solvents (water/acetic acid mixtures, methanol, acetone, dimethyl sulfoxide, and dimethylformamide) showed that the acetate bridges were broken in these solvents also. It is clear that the equilibrium concentration of the acetate-bridged complex **18** is always quite low, and that the crystallization of the potassium salt from the acetic acid/water mixture was driven by the low solubility of the compound in this medium.

When the solution obtained from reaction of **1** with acetic acid/water under argon was heated further (>60 min), the solution became brown-orange. The only peaks present in the ^{195}Pt NMR spectrum from platinum(II) complexes were very weak, from *cis*-$[Pt(NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**). There was also a weak doublet of triplets in the Pt^{IV} region of the ^{195}Pt NMR spectrum at 2619 ppm, with the triplet coupling at 517 Hz and the doublet coupling at 560 Hz. A value of 517 Hz for J(Pt^{IV}−N) is higher than expected for mutually trans nitrite-*N* ligands.[1,20] The Pt−N coupling trans to acetate would be expected to be less than trans to H_2O, so this resonance was assigned to *fac*-$[Pt(^{15}NO_2)_3(O_2CCH_3)_2(H_2O)]^-$ (**21**). The ^{15}N NMR spectrum showed singlets with satellites at 340 ppm (trans to acetate, J(Pt−N) = 517 Hz) and 325 ppm (trans to water, J(Pt−N) = 560 Hz). Related species with different numbers of acetate ligands bound were probably also present, with peaks too weak to be observed.

The major peaks in the ^{195}Pt NMR spectrum of this solution (with [^{14}N]nitrite) were two broad singlets ($\Delta\nu_{1/2}$ of approximately 300 Hz) at +874 and +1027 ppm. When the nitrite ligands were highly enriched in ^{15}N, these resonances appeared as similar multiplets; that at 1027 ppm is shown in Figure 2. It is a 1:2:1 triplet, with two weaker peaks halfway between the central and outer lines of the triplet. It is unlikely that there was an exact superposition of a separate doublet on a triplet at both chemical shifts. A pattern of this type cannot be obtained through ^{195}Pt−^{15}N coupling in a mononuclear complex but can easily be explained in terms of a dinuclear complex containing a Pt^{III}−Pt^{III} bond, with each Pt atom bound by two equivalent [^{15}N]nitrite ligands. If the two Pt atoms are equivalent, isotopomers ii and iii in Table 2 are identical, and each Pt-atom would give a 1:2:1 triplet. Isotopomer iv, with both Pt atoms having spin, would give in the ^{195}Pt NMR spectrum the X part of an $A_2A'_2XX'$ spectrum. If $J_{AX'}$ ($^2J(^{15}N-Pt-^{195}Pt)$) and $J_{AA'}$ ($^3J(^{15}N-Pt-Pt-^{15}N)$) were both close to zero and $J_{XX'}$ (J(Pt−Pt)) $\gg J_{AX}$ ($^1J(^{195}Pt-^{15}N)$), this spectrum would have the appearance of a ("deceptively simple") 1:4:6:4:1 quintet, with the line separation $^1/_2J_{AX}$ (*i.e.*, $^1/_2(^1J$(Pt−N))).[41] The value of ^1J(Pt−N) may be measured directly from the triplet separation (561 Hz). Some values of ^1J(Pt−Pt) for Pt(III) complexes are as follows: $[ClPt(\mu\text{-}SO_4)_4Pt(H_2O)]^{3-}$, 3464 Hz;[7] $[ClPt(\mu\text{-}HPO_4)_4(H_2O)]^{3-}$, 5342 Hz;[7] and in the acetate-bridged species **22** discussed below, 6800 Hz. Thus, it appears that J(Pt−Pt) is likely to be approximately ten times the magnitude of ^1J(Pt−N). The condition that $J_{XX'} \gg J_{AX}$ is therefore met. The observed spectrum will be the probability-weighted sum of the spectra from each of the isotopomers, giving a triplet superimposed on a quintet.

From the observation of a "triplet plus quintet" pattern, the presence of two Pt$^{III}(^{15}NO_2)_2$ moieties connected by a metal−metal bond may be inferred. We propose that there are also two bridging acetate ligands spanning the metal−metal bond. We have no direct evidence for this (potentially useful techniques, such as ^{13}C NMR could not be applied in the reaction medium containing a large excess of acetic acid). The presence of two acetate bridges is proposed on the following grounds:

(i) Most dinuclear Pt(III) compounds have two or more bridging ligands. There are only two reports of dinuclear complexes without bridging ligands,[42,43] and we are aware of no examples of Pt(III) atoms linked by only one bridging ligand.

(ii) A platinum(II) complex which can plausibly be regarded as a precursor complex, **18**, has two bridging acetate ligands (see above).

(iii) The ultimate product of the reaction of **1** with $CH_3CO_2H/HClO_4/H_2O$ is $[\{(H_2O)Pt(\mu\text{-}CH_3CO_2)_2\}_2]^{2+}$ (**4**), with four bridging acetate ligands.[8,9] The compound discussed here is an intermediate in its formation.[9]

In the spectrum obtained under the experimental conditions described, the ratio of the intensities of the signals at 1027 and 874 ppm was approximately 5:2, but the relative proportions changed with the composition of the solution. If acetic acid was added so that the ratio of acetic acid to water was greater than 3:1, the signal at 1027 ppm predominated, while, with lower ratios, the signal at 874 ppm was stronger. These peaks have therefore been assigned respectively to the complexes with two acetate ligands (**19c**) and with two water molecules (**19a**), coordinated at the "axial" sites (Scheme 2). Peaks (singlets with satellites) were also observed in ^{15}N NMR spectra which could be assigned to these complexes: for **19a**, δ_N 332.6, J(Pt−N) = 574 Hz; for **19c**, δ_N 331.7, J(Pt−N) = 561 Hz. In each case, these represented the sum of the spectra from isotopomers i (central peak) plus ii and iii (satellites). The peaks from isotopomer iv were too weak to be observed in the ^{15}N NMR spectrum. The observation of only one main ^{15}N peak for each

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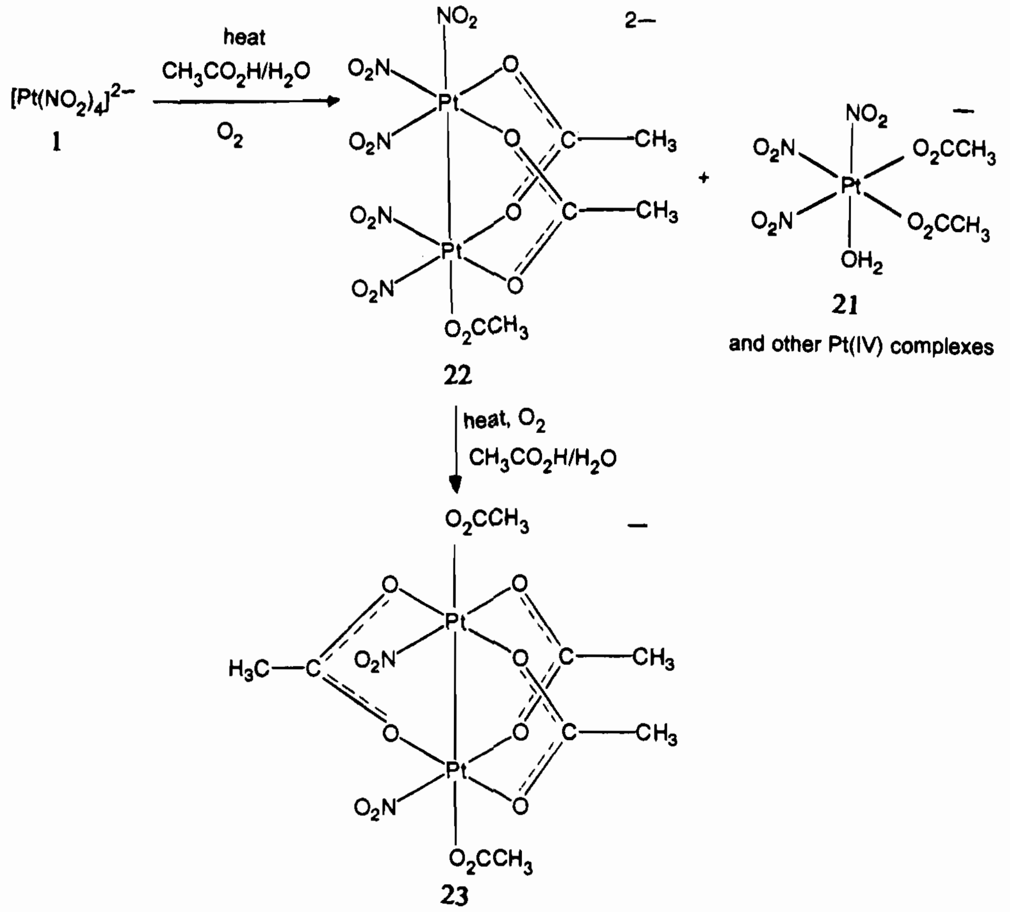
Scheme 3

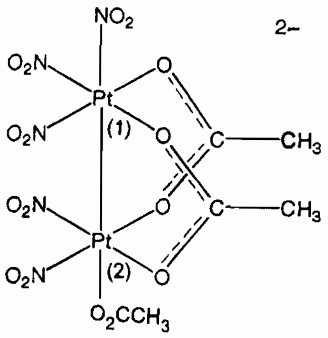


species was as expected if each of these complexes contained two acetate bridges (if only one bridge were present, the two ^{15}N atoms bound to each platinum atom would be nonequivalent).

Under some conditions, an additional set of weak peaks was also observed which were assigned to **19b**, an unsymmetrical complex with one axial acetate ligand, and one axial aqua ligand, in equilibrium with **19a** and **19c**. In this case, isotopomers ii and iii are different. With ^{15}N present, each gave a triplet pattern: at 1063 ppm, assigned to Pt bound by axial acetate (^{1}J(Pt–N) = 587 Hz), and at 776 ppm, assigned to Pt bound by axial water (^{1}J(Pt–N) = 546 Hz). Peaks from the less-abundant isotopomer iv were too weak to be observed, so the Pt–Pt coupling constant could not be measured.

Reactions of $K_2[Pt(NO_2)_4]$ (1) with Aqueous Acetic Acid under Air or Oxygen (Scheme 3). When oxygen or air was either bubbled through the reaction mixture or simply used as an atmosphere above the solution, the same series of color changes were observed as those under argon, but the changes occurred much more quickly. The initially colorless solution rapidly turned green and, within 5–10 min, had passed through yellow to a deep orange. Copious quantities of brown nitrogen dioxide were observed above the reaction mixture.

The ^{195}Pt NMR spectrum in the "platinum(III) region" of the orange solution (with [^{14}N]nitrite) (after 10 min of heating) is shown in Figure 3a. The major peaks were clearly due to an unsymmetrical dinuclear species, with two main peaks at 1319 (Pt$_{(2)}$) and 776 (Pt$_{(1)}$) ppm from isotopomers ii and iii and an AB pattern from the nonequivalent Pt atoms of isotopomer iv (^{1}J(Pt$_{(1)}$–Pt$_{(2)}$ = 6800 Hz). When ^{15}N was present (Figure 3b), each of the central peaks was split into a doublet of triplets. Each Pt atom therefore couples with two equivalent ^{15}N nuclei and one different ^{15}N nucleus. This pattern was as expected for a platinum(III) complex, **22**, with an axial nitrite bound to one Pt atom. The triplet splittings (^{1}J(Pt$_{(1)}$–N) = 617 Hz, ^{1}J(Pt$_{(2)}$–N) = 574 Hz) were as expected for "equatorial" nitrite ligands. The doublet splittings, from coupling with ^{15}N of axially bound nitrite, were 314 Hz for ^{1}J(Pt$_{(1)}$–N$_{ax}$) and 282 Hz for ^{2}J(Pt$_{(2)}$–Pt$_{(1)}$–N$_{ax}$). Previous work has shown that, unlike the equatorially bound N-atoms, the axially bound nitrite ^{15}N would be expected to couple to both Pt atoms. For example, in $[(O_2{}^{15}N)Pt_{(1)}(\mu\text{-}SO_4)_4Pt_{(2)}(H_2O)]^{3-}$, ^{1}J(Pt$_{(1)}$–N) = 314 Hz and ^{2}J(Pt$_{(2)}$–Pt$_{(1)}$–N) = 171 Hz.[7]



22

There was no direct evidence for the presence of either acetate or water as the other axial ligand, bound to Pt$_{(2)}$. Acetic acid concentration was high in these solutions, and addition of more acetic acid to the mixture did not cause any additional peaks to be observed. The species present was formulated as $[(O_2N)Pt_{(1)}(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt_{(2)}(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**), with axial

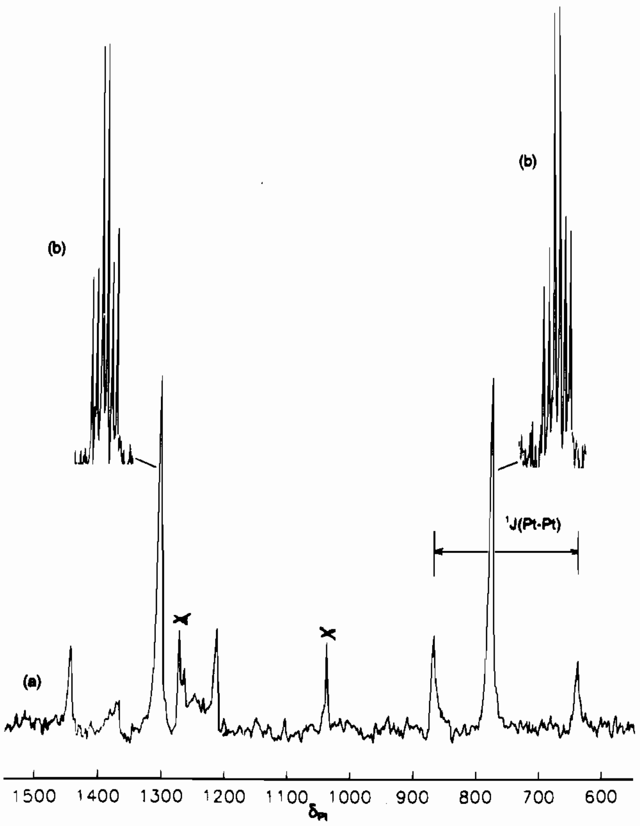


Figure 3. 21.4-MHz ^{195}Pt NMR spectrum in the Pt(III) region of a solution obtained by heating $K_2[Pt(NO_2)_4]$ with 3:1 acetic acid/water under oxygen. Except for peaks marked ×, peaks are due to $[\{(O_2N)Pt(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**): (a) with [^{14}N]-nitrite; (b) with [^{15}N]nitrite.

acetate. Peaks in the ^{15}N NMR spectrum (with satellites corresponding to the appropriate coupling constants) were observed for nitrite bound equatorially to $Pt_{(1)}$ (345.9 ppm) and $Pt_{(2)}$ (335.4 ppm) and for nitrite bound axially to $Pt_{(1)}$ (364.7 ppm, with two sets of satellites).

Only weak peaks (approximately 5% of the total intensity) were present from the symmetrical complex **19c**.

With further heating under air or oxygen (total time of 15–20 min), the solution became brown. Peaks from **22** were then weak. With [^{14}N]nitrite, the major peak in the "platinum(III) region" of the ^{195}Pt NMR spectrum was now a broad singlet ($\Delta\nu_{1/2} = 150$ Hz) at 1315 ppm. When [^{15}N]nitrite was present, the pattern observed was a doublet with a small singlet midway between the lines of the doublet. This pattern would be expected from a symmetrical platinum(III) complex with a metal–metal bond and only one ^{15}N-nitrite bound to each platinum atom. The two identical isotopomers ii and iii in Table 2 would each give a doublet from coupling of ^{195}Pt to one ^{15}N nucleus. The Pt–N coupling constant, 535 Hz, corresponded to an equatorial, rather than an axial nitrite ligand (see values for **19a–c** and for **22**, discussed above). The ^{195}Pt NMR pattern for isotopomer iv, with both Pt-atoms ^{195}Pt, would be the X-part of an AA′XX′ spectrum. If $J_{XX'} \gg J_{AX}$ (*i.e.*, $J(Pt_{(1)}-Pt_{(2)}) \gg {}^1J(Pt-N)$) and other coupling constants are close to zero, the X-part of this pattern will be a 1:2:1 triplet, with the line separation within the triplet corresponding to $^1/_2(J_{AX})$.[41,44] The overall ^{195}Pt NMR spectrum would therefore be a doublet superimposed on a triplet whose outer lines were coincident with those of the doublet, giving the appearance of doublet plus singlet. In the ^{15}N NMR spectrum, peaks from isotopomer iv were not observed, but peaks were observed from isotopomers i–iii, giving δ_N 320.1 ppm and confirming $^1J(Pt-N) = 535$ Hz.

From the observed pattern, it was therefore clear that these peaks were from a platinum(III) complex containing $O_2N-Pt-Pt-NO_2$. With less certainty, we propose that three bridging acetate ligands were also present, for similar reasons for the proposal above that two such bridges were present in **19a,c**. Further heating did not cause additional "doublet plus triplet" patterns to be observed with higher platinum resonance frequency. The species present in these solutions (which always contained high acetic acid concentrations) was also formulated as having acetate ligands coordinated axially, $[\{(CH_3CO_2)Pt(NO_2)\}_2(\mu\text{-}CH_3CO_2)_3]^-$ (**23**) (Scheme 3) (this formulation was supported by spectra of solutions obtained from reaction of $K_2[Pt(^{15}NO_2)_4]$ with $CH_3CO_2H/HClO_4/H_2O$, described elsewhere[9]).

Peaks were also observed in ^{195}Pt and ^{15}N NMR spectra from **21**, as well as weaker peaks in the platinum(IV) region of these spectra, which were not confidently assigned to particular complexes or studied in detail.

Reactions of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ with CH_3CO_2H/H_2O under Various Conditions (Scheme 4). The results described above showed that reactions of $K_2[Pt(NO_2)_4]$ with acetic acid/water gave mixtures of Pt(II), Pt(III), and Pt(IV) complexes. While the particular complexes formed, and the rates of the reactions were dependent on the reaction conditions, it was noteworthy that, even under argon, oxidation of Pt(II) to these higher oxidation states occurred. To throw additional light on the reaction pathways involved, we decided to react a preformed solution of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**) with aqueous acetic acid under various conditions. This allowed the reactions of dinitritoplatinum(II) complexes to be studied in the absence of products (HNO_2, HNO_3, and NO_2) formed from the reactions of the nitro groups of $K_2[Pt(NO_2)_4]$ or in the presence of one of these compounds deliberately added.

The formation of *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**) in solution by reaction of 2 mol equiv of sulfamic acid with $K_2[Pt(NO_2)_4]$ is now well-established.[45,46] The solution also usually contained small proportions of $[Pt(NO_2)_3(H_2O)]^-$ (**6**).[1] In each case, glacial acetic acid was added to an aqueous solution of **7** until the volume ratio of acetic acid/water was 3:1.

When a solution prepared using ^{15}N-labeled nitrite was heated briefly under argon, the ^{195}Pt NMR spectrum showed peaks due to *cis*-$[Pt(^{15}NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**) with much weaker peaks from $[\{Pt(^{15}NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**18**) and $[Pt(^{15}NO_2)_3(O_2CCH_3)]^{2-}$ (**15**). Continued heating caused the formation of a green color, with little change in the ^{195}Pt NMR spectrum. Only a very weak set of peaks from the Pt(III) complex **19c** was observed.

When a similar solution was heated at 90 °C in air or oxygen, the ^{195}Pt NMR spectrum after a short time (15–20 min) showed peaks predominantly due to the symmetrical Pt(III) complex $[\{(CH_3CO_2)Pt(^{15}NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**19c**) (Scheme 5). Sometimes, weak peaks from **19b**, with one axial water ligand, were also present. With further heating, peaks assigned to $[\{(CH_3CO_2)Pt(^{15}NO_2)\}_2(\mu\text{-}CH_3CO_2)_3]^-$ (**23**) grew rapidly. Weak peaks were also present in the platinum(IV) region.

While this experiment showed that oxygen was an efficient oxidant for conversion of Pt(II) to Pt(III) complexes under appropriate conditions, we had not yet identified the oxidant present under anaerobic conditions. An experiment was there-

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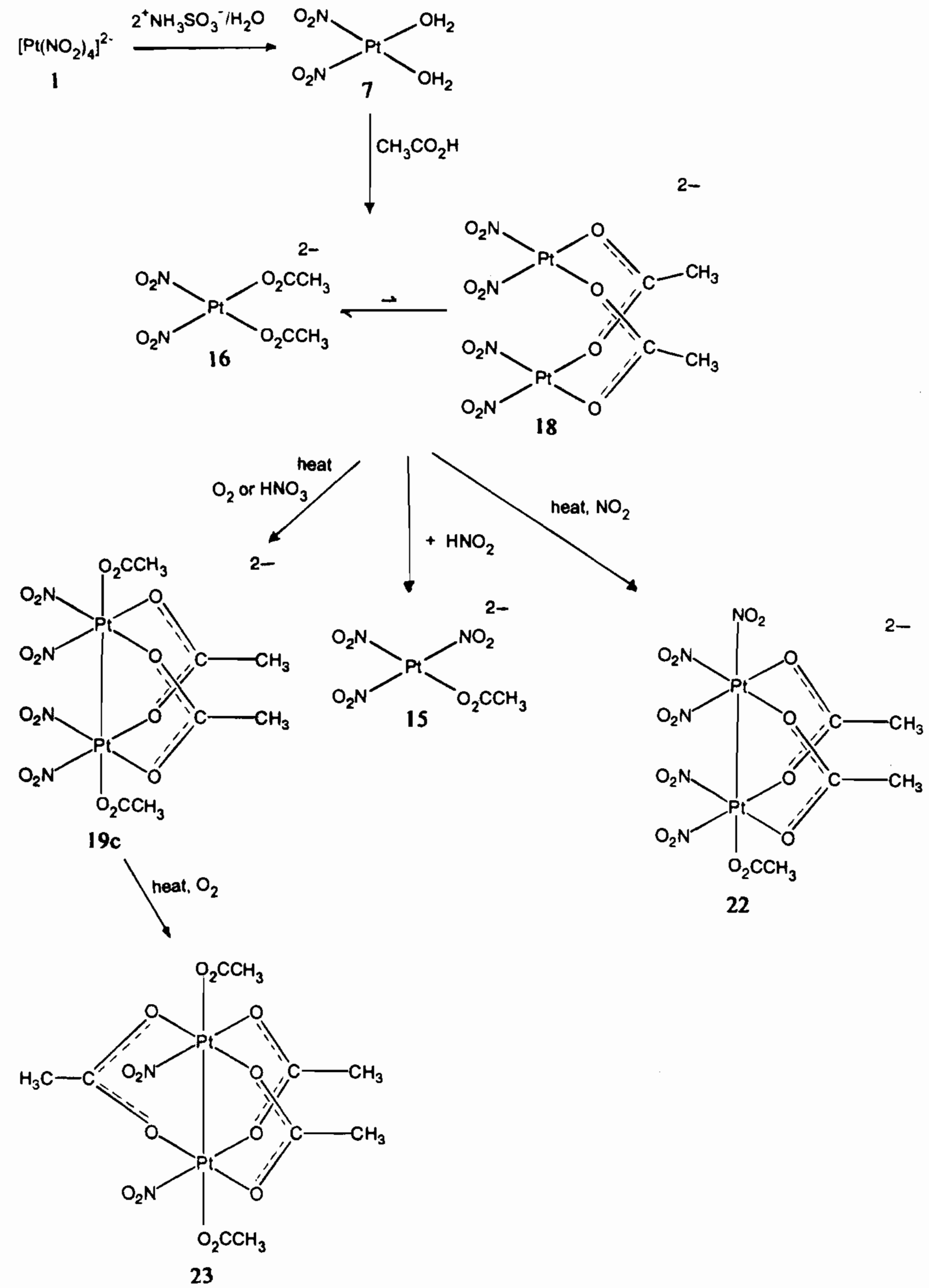
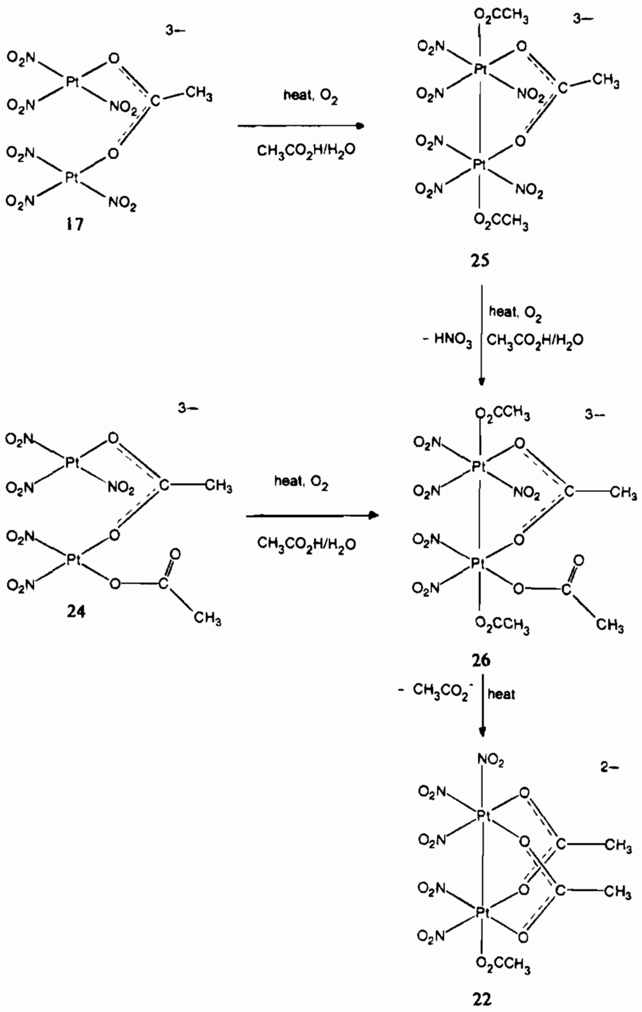
Scheme 4



fore carried out in which 1 M aqueous nitric acid was added in aliquots to the reaction mixture under argon during the heating process. At times 2, 20, and 40 min after heating at 90 °C began, 1 mol equiv (with respect to moles of platinum present) of nitric acid was added. The solution quickly passed through a green stage (1−5 min) to a yellow color. The ^{195}Pt NMR spectrum of this solution showed peaks from the Pt(II) complex *cis*-[Pt(^{15}NO$_2$)$_2$(O$_2$CCH$_3$)$_2$] (**16**) and the Pt(III) complex [{CH$_3$CO$_2$)Pt(^{15}NO$_2$)$_2$(μ-CH$_3$CO$_2$)}$_2$]$^{2-}$ (**19c**). After 25 min, 5 min after addition of the second aliquot of HNO$_3$, no peaks from Pt(II) complexes were observed in the ^{195}Pt NMR spectrum, only peaks from **19c** and weak peaks from Pt(IV) complexes. With further heating (and another addition of HNO$_3$), peaks due to **19c** slowly decreased in intensity while those from [{(CH$_3$CO$_2$)Pt(^{15}NO$_2$)}$_2$(μ-CH$_3$CO$_2$)$_3$]$^-$ (**23**) grew. This experiment showed that nitric acid can efficiently oxidize the Pt(II) precursors to Pt(III) under anaerobic conditions.

A solution of H^{15}NO$_2$ was prepared by addition of 1.1 mL of ice-cold degassed 1 M HClO$_4$ solution to 0.075 g of Na^{15}NO$_2$ under argon. The HNO$_2$ solution was added in three portions (each corresponding to 1 mol equiv) at similar times to the additions of HNO$_3$ solution described above. After 20 min of heating, and the second addition of HNO$_2$ solution, the ^{195}Pt NMR spectrum of the solution showed peaks from *cis*-[Pt(^{15}NO$_2$)$_2$(O$_2$CCH$_3$)$_2$] (**16**) and [Pt(^{15}NO$_2$)$_3$(O$_2$CCH$_3$)]$^{2-}$ (**15**). The trinitro complex **15** was evidently formed by coordination of some of the added nitrite. With further heating and an additional aliquot of HNO$_2$ solution (total heating time 45 min), the spectrum still showed predominatly peaks due to these Pt(II) species but with a weak additional peak from the Pt(III) complex **19c**. There was little further change with prolonged heating, except that the peaks from **19c** decreased slightly in intensity while peaks from **23** were detected. The effect of addition of HNO$_2$ was therefore chiefly to provide nitrite ligand

Scheme 5



to coordinate to Pt(II) and probably also to be the source of a little nitric acid from reaction (5), which would oxidize some Pt(II) to Pt(III).

None of the results described above could account for the formation under aerobic conditions of the unsymmetrical Pt(III) complex with axial nitrite, $[(O_2N)Pt(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**). We considered the possibility that **22** might be formed through reaction of Pt(II) precursors with nitrogen dioxide, which was certainly present when the reaction was carried out in air, presumably mainly from reaction of NO with oxygen (reactions 5 and 6). To test this possibility, NO_2 was passed in a stream of argon slowly through the heated reaction mixture from the di(nitrito-*N*)platinum(II) complex in acetic acid/water (see Experimental Section). The reaction was carried out both with [^{14}N]- and [^{15}N]nitrite in the starting materials. In the ^{195}Pt NMR spectra of the resultant solutions, the strongest peaks were from the platinum(III) complex with axial nitrite, **22**. There were also much weaker peaks from **19c**. It was therefore clear that NO_2 oxidation of Pt(II) precursors was a route to **22**, with **19c** formed in this solution by subsequent loss of axial nitrite from **22** and/or by independent oxidation of Pt(II) complexes by HNO_3 formed by reaction of NO_2 with water.

Reactions of $[Pt(NO_2)_3(H_2O)]^-$ with CH_3CO_2H/H_2O under Various Conditions. Solutions of $[Pt(NO_2)_3(H_2O)]^-$ (**6**), usually mixed with smaller amounts of $[Pt(NO_2)_4]^{2-}$ and *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (**7**) could be prepared by careful reaction of $K_2[Pt(NO_2)_4]$ (**1**) with 1 mol equiv of sulfamic acid.[1] As with the solutions of the dinitrito complex discussed above, acetic acid was added to the aqueous solution and the reaction mixture heated under various conditions.

Under argon, ^{195}Pt NMR peaks from $[Pt(^{15}NO_2)_3(O_2CCH_3)]^{2-}$ (**15**) and *cis*-$[Pt(^{15}NO_2)_2(O_2CCH_3)_2]$ (**16**) were observed, and, after prolonged heating, very weak peaks from the Pt(III) complexes **19a,c**. The solution remained yellow green.

Under oxygen, the solution turned green within 2 min from commencement of heating at 90 °C, then turned to yellow within 10 min. The major peaks in the ^{195}Pt NMR spectrum were from the Pt(II) complexes **15** and **16**, with much weaker peaks from the acetate-bridged complexes **17** and **18**. With further heating, the major species was the asymmetric Pt(III) complex $[(O_2N)Pt(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**). The symmetric Pt(III) complex **19c** was present as a minor product. After prolonged heating, the only Pt(III) complex whose peaks were detected in the ^{195}Pt NMR spectrum was **23**. Peaks from the trinitritoplatinum(IV) complex **21** were also present, together with weaker peaks in this region of the ^{195}Pt NMR spectrum. The amount of NO_2 generated from reaction of Pt$-NO_2$ with acid would not be sufficient in this case to allow for the formation of the large amounts of **22** observed solely through oxidation of Pt(II) complexes with NO_2. From these results, it therefore appears that an alternative route to **22** is by oxidation (with O_2 and perhaps also HNO_3) of a trinitritoplatinum(II) precursor.

Discussion

Reaction Pathways in Reaction of Platinum(II) Nitrite Complexes with Aqueous Acetic Acid. From the results reported above, we are able to propose reaction pathways which lead to the mixed nitrito/acetatoplatinum(III) complexes **19**, **22**, and **23**. In acetic acid/water mixtures, these reactions do not lead to a platinum(III) acetate, which does not contain any nitrite, but, as described elsewhere,[8,9] addition of a strong acid with a noncoordinating anion (perchloric or triflic) does give the nitrite-free product, $[\{(H_2O)Pt(\mu\text{-}CH_3CO_2)_2\}_2]^{2+}$ (**4**). The weak acid strength of acetic acid allowed compounds to be detected in this system which are doubtless analogous to intermediates that have not so far been detected in the formation of the sulfate- or phosphate-bridged platinum(III) complexes **2** and **3** from reaction of **1** with these stronger acids. The reaction pathways outlined below for acetate complexes would therefore be expected to be similar to those involved in the formation of platinum(III) complexes in the sulfuric and phosphoric acid solutions.

Step 1: Reaction of Pt(II)$-NO_2$ with Acid. This produces a vacant coordination site on Pt(II) which can then be occupied by acetate. In the absence of oxygen, the initial product of the reaction is HNO_2, which disproportionates to HNO_3 and NO (eq 5). In the presence of oxygen, the cleavage of $Pt^{II}-NO_2$ and formation of HNO_3 are faster, and some NO_2 also forms.

Step 2: Oxidation of Mononuclear Platinum(II) Complexes to Platinum(IV). We propose that oxidation of a mononuclear Pt(II) complex by HNO_3 or O_2 usually leads to a mononuclear Pt(IV) complex. The most abundant Pt(IV) products have facial trinitrito groups, probably formed through oxidation of trinitritoplatinum(II) complexes. This represents a "side reaction" which decreases the yield of Pt(III) complexes.

Step 3: Formation of Dinuclear Acetate-Bridged Platinum(II) Complexes. As shown above, relatively small proportions of the dinuclear complexes **17** and **18** are present in equilibrium with mononuclear platinum(II) complexes.

Step 4: Oxidation of Dinuclear Acetate-Bridged Platinum(II) Complexes to Platinum(III) Complexes. We propose that the proximity of the two metal atoms in the dinuclear platinum(II) complexes causes them to be oxidized readily to dinuclear platinum(III) complexes containing a metal$-$metal bond. There is then a competition between oxidation of mononuclear Pt(II) complexes to Pt(IV) and of dinuclear Pt(II) complexes to Pt(III). Although the dinuclear Pt(II) complexes are present only in relatively small proportions, their more facile oxidation causes formation of Pt(III) complexes to be always an important reaction pathway and, under milder oxidation conditions, the dominant pathway. Details of the oxidation reactions will be discussed further below.

Step 5: Displacement of Coordinated Nitrite from Platinum(III) Dinuclear Complexes and Formation of Additional Acetate Bridges. With heating in the acidic medium, nitrite ligands bound to Pt(III) are removed, in reactions analogous to those proposed in step 1 above. Once again, this occurs much more readily when oxygen is present. These reactions produce more nitric acid, which can oxidize Pt(II) complexes still present in the solution. The coordination sites created will be occupied by acetate, and, ultimately, an "equatorial" acetate will form an additional bridge between the Pt(III) atoms. This process continues to the formation of **23**, with three bridging acetate ligands.

Oxidation of Platinum(II) Precursors to Platinum(III) Complexes. The crucial step in formation of the platinum(III) dinuclear complexes is step 4 above. As described in the Results, a solution containing $[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**18**) in equilibrium with *cis*-$[Pt(NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**) in aqueous acetic acid may be heated under argon with little change. With nitric acid under argon, or in the presence of dioxygen, the platinum(III) complex $[\{(CH_3CO_2)Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**19c**) formed readily. We do not have any evidence that would allow us to make definitive comments about the mechanisms of these oxidations. It may suffice here to note that oxidation of a (Pt^{II}_2) unit to (Pt^{III}_2) formally requires removal of two electrons, which could be accomplished by conversion of O_2 to O_2^{2-}, or of HNO_3 to HNO_2 (which would be followed by regeneration of more HNO_3 by reaction 5). Any weak attraction between the Pt atoms in a Pt(II) dinuclear complex, as suggested above, may help the reaction to proceed.

The nitrite ligands bound to platinum(II) precursors appear also to be important in modulating the redox potentials of the complexes to facilitate oxidation to platinum(III) products. A possible preparative route would appear to be oxidation of solutions obtained from $[Pt(H_2O)_4]^{2+}$ and anions such as acetate or sulfate. Although platinum(II) complexes with these anions coordinated form readily,[19] reactions with oxidants such as O_2 and HNO_3 under a wide variety of conditions did not produce any platinum(III) products detectable by NMR spectroscopy.[47]

When a solution containing initially $[Pt(NO_2)_3(O_2CCH_3)]^{2-}$ (**15**) in equilibrium with $[\{Pt(NO_2)_3(\mu\text{-}CH_3CO_2)\}_2]^{3-}$ (**17**) (and with small amounts of $K_2[Pt(NO_2)_4]$ (**1**) and *cis*-dinitritoplatinum(II) complexes also unavoidably present) was heated under oxygen, $[(O_2N)Pt(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**), with one axially coordinated nitrite, was the major Pt(III) product. Although we have shown that such complexes may be formed by reaction of dinuclear Pt(II) complexes with NO_2 (see below), there would not be sufficient NO_2 present in this reaction mixture to account for the amount of **22** produced (NO_2 would only be generated from reactions 1, 3, and 4). We propose that oxidation of $[\{Pt(NO_2)_3(\mu\text{-}CH_3CO_2)\}_2]^{3-}$ (**17**) or $[Pt(NO_2)_3(\mu\text{-}CH_3CO_2)Pt(NO_2)_2(O_2CCH_3)]^{3-}$ (**24**) gives initially a Pt(III) product (**25** or **26**, respectively) which contains one bridging acetate (Scheme 5). It is quite possible that **24** is more readily oxidized than **17**, but it would be expected that if **25** were produced, equatorial nitrite would be easily replaced by acetate to give **26**. If an equatorial nitrite then migrates to the axial coordination site (displacing weakly bound axial acetate), it is possible for a second acetate bridge to form between the Pt atoms, giving **22** (Scheme 5). Peaks from the proposed intermediates **24**–**26** have not been identified in our spectra.

An alternative route to **22** is by reaction of a solution containing $[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$ (**18**) in equilibrium with *cis*-$[Pt(NO_2)_2(O_2CCH_3)_2]^{2-}$ (**16**) with NO_2 under argon. The NO_2 is converted to the axially coordinated nitrite in **22** and is therefore a one-electron oxidant. Reaction of **18** with 1 mol of NO_2 would produce a dinuclear mixed-valence compound $[(O_2N)Pt^{III}(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt^{II}(NO_2)_2]^{2-}$. This paramagnetic species would not be detectable by NMR. Some HNO_3 would be present from reaction of NO_2 with water, and it may be that the Pt(II) is very easily oxidized by small amounts of HNO_3, to give $[(O_2N)Pt^{III}(NO_2)_2(\mu\text{-}CH_3CO_2)_2Pt^{III}(NO_2)_2(O_2CCH_3)]^{2-}$ (**22**). Alternatively, excess NO_2 might react with the Pt(II) atom in the mixed-valence complex to give a dinuclear platinum(III) complex with two axial nitrite ligands, $[\{(O_2N)Pt^{III}(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]^{2-}$. Peaks from this species were not identified in our spectra. They may not be readily detectable in ^{195}Pt NMR spectra of ^{15}N-enriched compounds because the ^{15}N nuclei of the two axially coordinated $^{15}NO_2^-$ ligands would be magnetically nonequivalent in isotopomers containing one or two ^{195}Pt nuclei, giving second order patterns with dispersal of the signal among many peaks. There is ample evidence that the trans influence of a ligand coordinated axially in a Pt(III) dinuclear complex can operate through the metal–metal bond,[7,48] which would facilitate removal of one of the two axial nitrite ligands to give **22**.

In the reaction of $K_2[Pt(NO_2)_4]$ (**1**) with aqueous acetic acid under argon, conditions are only mildly oxidizing, and only **18**, containing dinitritoplatinum(II) groups, is likely to be significantly oxidized to a Pt(III) dimer, so the reaction proceeds to **19c**. But under oxygen or air, the major Pt(III) product is **22**. With more strongly oxidizing conditions, oxidation of dimers containing trinitritoplatinum(II) groups, **17** and **24**, may occur in competition with the removal of nitrite bound to Pt(II). The reactions outlined in Scheme 5 would then lead to **22**. Nitrogen dioxide is also present under these conditions (observed as a brown gas above the reaction mixture), so that oxidation of Pt(II) complexes by NO_2 may also be competing routes to **22**.

Conclusion

The reaction of nitritoplatinum(II) complexes with the appropriate acid remains the only method that can be used to prepare the platinum(III) complexes **2**–**4**. From our results, it appears that the formation of these interesting compounds is dependent on a fine balance of equilibrium constants for dinuclear platinum(II) complexes, redox potentials of the different platinum(II) complexes and available oxidants, and relative rates of a number of complex competing reactions. It is unlikely that this synthetic method would ever have been developed *de novo* as a "rational synthesis".

Acknowledgment. We thank the Australian Research Council and the Queensland Cancer Fund for financial support and Dr. G. Hanson of the Centre for Magnetic Resonance at this University for running EPR spectra.

Supporting Information Available: Tables of full crystallographic data, all bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and a packing diagram for $K_2[\{Pt(NO_2)_2(\mu\text{-}CH_3CO_2)\}_2]\cdot H_2O$ (5 pages). Ordering information is given on any current masthead page.

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