Hydrogen-Bonding Patterns in Oxime/Oximato Platinum(II) Species Providing the Formation of One-Dimensional Chains, Two-Dimensional Networks, and Cages

Vadim Yu. Kukushkin,*,†,‡ Takanori Nishioka,§ David Tudela,*,‖ Kiyoshi Isobe,*,§ and Isamu Kinoshita§

Department of Chemistry, St. Petersburg State University, 198904 Stary Petergof, Russian Federation, Faculty of Science, Department of Material Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan, and Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Heating *cis*-[PtCl₂(Me₂C=OH)₂] in molten 2-propanone oxime affords the cationic complex [PtCl(Me₂C=NOH)₃]-Cl. This compound reacts with 1 equiv of NaOH to give the neutral complex *cis*-[PtCl(Me₂C=NO)(Me₂C=NOH)₂] (**1**). Further, the reaction of [PtCl(Me₂C=NOH)₃]Cl with 2 equiv of AgNO₃ and successive addition of excess oxime and NaSbF₆ afford the chloride-free cationic complex [Pt(Me₂C=NO)(Me₂C=NOH)₃](SbF₆). When a solution of NaOH, instead of NaSbF₆, was added to the reaction mixture, the neutral compound [Pt(Me₂C=NO)₂-(Me₂C=NOH)₂]·2H₂O (**2**) was isolated. The homoleptic complex [Pt(Me₂C=NOH)₄]Cl₂ (**3**) was prepared both by addition of excess HCl to [Pt(Me₂C=NO)₂(Me₂C=NOH)₂] (87% yield) and by prolonged heating of [PtCl-(Me₂C=NOH)₃]Cl and excess 2-propanone oxime, although in the latter case the conversion of the starting complex did not exceed 5−10%. **1**−**3** were characterized by X-ray diffraction. All three compounds display interesting hydrogen-bonding modes. In **1**, two crystallographically independent molecules of *cis*-[PtCl(Me₂C=NO)-(Me₂C=NOH)₂] form the repeat unit for a novel type of self-assembly that produces infinite one-dimensional polymeric chains held by strong H-bonds. **2**, as compared to *vic*-dioxime Pt(II) complexes, displays stronger intramolecular hydrogen bonds and shows the absence of columnar stacking. In addition, the solvation H₂O molecules connect the Pt(II) building elements by intermolecular H-bonds to form a layered two-dimensional network. In **3**, the counterion is involved in (μ_4-Cl⁻)·*cis*-[(···H−O−)₂(···H−CH₂−)₂] hydrogen bonding, thus forming the caged complex. Another interesting structural feature of **3** is the interaction between methyl hydrogens and platinum.

Introduction

The hydrogen bond is frequently used in designing supramolecular arrays.[1] A great deal of progress has been done in the construction of organic aggregates held by H-bonds.[1−3] The use of transition metal complexes for assembly or self-assembly by hydrogen bonding has received much less attention, although several elegant works[4−8] in this area are well-known. These examples include aggregates formed by cocrystallization of metal complexes with complementary organic molecules,[4] supramolecular assemblies involving organometallic free acids,[5]

supramolecular coordination compounds based on the copper(I) complexes [CuL₄]X (L = 3-cyano-6-methyl-2(1*H*)-pyridinone; X = ClO₄, BF₄, PF₆, CF₃SO₃) with a three-dimensional framework of tetrahedral CuN₄ centers linked by intermolecular hydrogen bonds through pyridone N and O atoms,[6] a tetrapyridylstannane complex containing four pyridone functionalities linked to neighboring molecules by pyridone−pyridone interactions involving hydrogen bonding,[7] organoplatinum complexes possessing hydrogen-bond donor and hydrogen-bond acceptor groups at either end of the molecules, separated by a rigid aryl spacer,[8a] and the platinum(II) complex [PtCl{C₆H₂(CH₂NMe₂)₂-2,6-(C≡CH)-4}] exhibiting a polymeric linear −C≡CH···Cl−Pt− hydrogen-bonded structure.[8b]

We report herein a new type of self-assembly involving oxime/oximato Pt(II) complexes that produces infinite one-dimensional polymeric chains held by hydrogen bonding. It

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* Corresponding authors.
† St. Petersburg State University. E-mail: kukushkin@vk2100.spb.edu.
‡ Visiting Professor of the Osaka City University.
§ Osaka City University. E-mail: isobe@cubane.sci.osaka-cu.ac.jp.
‖ Universidad Autónoma de Madrid. E-mail: david.tudela@uam.es.
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was also found that water molecules can connect some oxime/oximato Pt(II) building elements to form a layered two-dimensional network. Furthermore, we observed an unusual type of hydrogen bonding, *i.e.* $(\mu_4\text{-Cl}^-)\cdot cis\text{-}[(\cdots\text{H}-\text{O}-)_2(\cdots\text{H}-\text{CH}_2-)_2]$ within an oxime complex. All the above mentioned results are included in the paper.

In this study, we have used the tris(2-propanone oxime) complex of platinum(II), $[\text{PtCl}(\text{Me}_2\text{C}=\text{NOH})_3]^+$, as a starting material for building elements to design polymeric chains of complexes. This complex was selected for the following reasons: (i) The *N*-coordination of 2-propanone oxime (pK_a in water is 12.4[9]) to a platinum(II) center leads to a dramatic decrease of pK_a values (by 4−8 units[10]) and brings about easy transformation of the oxime ligand into oximato species. Thus, the conjugate acid and base, which are coordinated to the Pt-(II) ion, may be present in the same complex. Therefore, the formation of H-bonding between protons of the OH groups of coordinated oximes and oximato oxygen(s) can be expected. Indeed, the negative charge on the oximato oxygen atoms places these compounds in one of the three fundamental types[11] of strong and very strong hydrogen bonds, *i.e.* the so-called *negative charge assisted hydrogen bonding*. (ii) The complex $[\text{PtCl}(\text{Me}_2\text{C}=\text{NOH})_3]\text{Cl}$ [$K_{a1} = (3.0 \pm 0.2) \times 10^{-4}$ and $K_{a2} = (1.9 \pm 0.2) \times 10^{-4}$; K_{a3} was not determined[12]] is deprotonated in a pH range where the compound is stable toward hydrolysis. (iii) In contrast to the structurally rigid coordinated *vic*-dioxime ligands, 2-propanone oxime has flexibility around the Pt−N bond. This, in turn, might lead to (a) increased tendency toward the formation of *inter-* rather than *intra*molecular hydrogen bonding and (b) decreased probability for the columnar stacking of complexes in the crystal—the characteristic phenomenon for complexes with coordinated *vic*-dioximes[13,14]—due to the steric hindrance of the =CMe$_2$ groups. (iv) $[\text{PtCl}(\text{Me}_2\text{C}=\text{NOH})_3]\text{Cl}$ offers broad possibilities for derivatization by deprotonation and substitution reactions of coordinated Cl$^-$.

Experimental Section

Materials and Instrumentation. K$_2$[PtCl$_4$] was recrystallized from water before use. *cis*-[PtCl$_2$(Me$_2$C=NOH)$_2$] was synthesized by the published method[15] from K$_2$[PtCl$_4$] and excess Me$_2$C=NOH. All other chemicals and solvents were obtained from commercial sources and were used as received. C, H, and N elemental analyses were carried out by the Microanalytical Service, Osaka City University. FAB and EI mass spectra were obtained with VG Autospec and JEOL JMS-AX500 instruments. Melting and decomposition points were determined in capillary. DTA/TG measurements were performed in air on Perkin-Elmer DTA 7 and TGA 7 instruments. For TLC, Riedel-deHaën 60 F 254 SiO$_2$ plates with layer thickness 0.2 mm were used. Infrared

spectra (4000−220 cm^{-1}) were recorded on a Perkin-Elmer 1650 FT-IR instrument, using Nujol and perfluorohydrocarbon oil mulls between CsI windows. ^{1}H NMR spectra were recorded at room temperature on Bruker AMX-300 and JEOL JNM-LA300WB instruments.

Synthetic Work and Characterization. [PtCl(Me$_2$C=NOH)$_3$]Cl. A finely ground mixture of *cis*-[PtCl$_2$(Me$_2$C=NOH)$_2$] (1.98 g, 4.8 mmol) and 2-propanone oxime (1.40 g, 19.2 mmol) and 1 mL of nitromethane are placed in a 50-mL round-bottomed flask, equipped with a Teflon-coated magnetic stirring bar and reflux condenser connected to a CaCl$_2$ tube. The mixture is stirred for 15 min, while the temperature is raised from 25 to 100 °C, and the bright yellow suspension of the starting materials is gradually transformed into a yellow solution, followed by immediate formation of a precipitate. Sometimes, the formation of the solution is not observed and the starting suspension is directly converted into a new one.

The reaction mixture is then kept at 100 °C for 30 min and cooled to 20−25 °C. After that, a mixture of 10 mL of chloroform and 10 mL of hexane is added and the suspension formed is stirred at room temperature for 15 min. The white precipitate is collected on a filter, washed with two 3-mL portions of chloroform and two 5-mL portions of diethyl ether, and dried in air at room temperature. The yield of [PtCl(Me$_2$C=NOH)$_3$]Cl is 1.64 g, 70%. Anal. Calcd for C$_9$H$_{21}$-Cl$_2$N$_3$O$_3$Pt: C, 22.28; H, 4.36; N, 8.66. Found: C, 22.30; H, 4.34; N, 8.40. FAB$^+$-MS, *m/z*: 450 ([PtCl(Me$_2$C=NOH)$_3$]$^+$). The complex is obtained as a white powder. [PtCl(Me$_2$C=NOH)$_3$]Cl decomposes partially on dissolution in acetone or nitromethane at room temperature in the absence of excess ligand, to give *trans*-[PtCl$_2$(Me$_2$C=NOH)$_2$] and free 2-propanone oxime. An aqueous solution of [PtCl-(Me$_2$C=NOH)$_3$]Cl (*ca.* 10^{-3} M) is stable for a few hours, but slow release of fine needle-like yellow crystals of *trans*-[PtCl$_2$(Me$_2$C=NOH)$_2$] is observed after 2 days of standing at room temperature. When [PtCl-(Me$_2$C=NOH)$_3$]Cl is heated in the solid state at 170−175 °C, elimination of one oxime ligand and formation of *trans*-[PtCl$_2$-(Me$_2$C=NOH)$_2$] are observed. Principal features of DTA/TG (heating rate 2 °C min^{-1}): 165−175 °C endothermic peak (mass loss 15.3%; calcd mass loss for the elimination of one 2-propanone oxime ligand is 15.1%). IR data, cm^{-1}: 1671 w ν(C=N), 342 s ν(Pt−Cl). ^{1}H NMR in D$_2$O, δ: 2.21 (3 H), 2.22 (6 H), 2.60 (3 H), 2.66 (6 H). ^{1}H NMR in D$_2$O/CF$_3$CO$_2$H, δ: 2.29 (9 H), 2.66 (3 H), 2.71 (6 H).

***cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$].** A 1.1-mL portion of 1 M NaOH is added at room temperature to a solution of 0.53 g (1.1 mmol) of [PtCl(Me$_2$C=NOH)$_3$]Cl in water (12 mL). The white solid, which appears a few seconds after the addition, is collected on a filter, washed with two 1-mL portions of water, and dried in air. The yield of *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] is 0.28 g, 58%. In contrast to [PtCl-(Me$_2$C=NOH)$_3$]Cl, *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] is poorly soluble in water at room temperature but readily soluble in methanol. Anal. Calcd for C$_9$H$_{20}$ClN$_3$O$_3$Pt: C, 24.09; H, 4.49; N, 9.36. Found: C, 24.62; H, 4.59; N, 9.46. EI-MS, *m/z*: 449 (M)$^+$. Mp = 163−165 °C. TLC on SiO$_2$, CHCl$_3$:Me$_2$CO = 1:1: R_f = 0.62. IR data, cm^{-1}: 1676 m, br ν(OH), 1614w , 1544 m, 1537 m ν(C=N), 344 w, 337 w ν(Pt−Cl). ^{1}H NMR in CD$_3$OD, δ: 2.05 (3 H), 2.12 (6 H), 2.21 (3 H), 2.53 (6 H). ^{1}H NMR in CD$_3$OD/CF$_3$CO$_2$H, δ: 2.22 (6 H), 2.23 (3 H), 2.63 (3 H), 2.68 (6 H). A crystal for X-ray study was obtained by slow evaporation of an aqueous solution.

[Pt(Me$_2$C=NO)(Me$_2$C=NOH)$_3$][SbF$_6$]. Silver nitrate (0.37 g, 2.2 mmol) is added to a solution of [PtCl(Me$_2$C=NOH)$_3$]Cl (0.51 g, 1.1 mmol) in water (12 mL), and the reaction mixture is stirred in the dark at room temperature for 48 h. AgCl is filtered off, and 2-propanone oxime (0.77 g, 10.5 mmol) is added to the filtrate, whereafter the solution is left to stand at room temperature for 24 h. Solid sodium hexafluoroantimonate, NaSbF$_6$ (0.54 g, 2.1 mmol), is then added to the reaction mixture, and the white precipitate formed is collected on a filter, washed with three 0.5-mL portions of water, and dried in air. The yield of [Pt(Me$_2$C=NO)(Me$_2$C=NOH)$_3$][SbF$_6$] is 0.59 g, 77%. The complex can be recrystallized from hot (80−90 °C) nitromethane. This operation should be carried out rapidly to prevent decomposition. Anal. Calcd for C$_{12}$H$_{27}$F$_6$N$_4$O$_4$PtSb: C, 19.96; H, 3.77; N, 7.76. Found: C, 19.45; H, 3.61; N, 7.55. FAB$^+$-MS, *m/z*: 486 ([Pt(Me$_2$C=NO)-(Me$_2$C=NOH)$_3$]$^+$). The complex crystallizes from nitromethane in the tetragonal space group *P4/nmm* with $a = b = 20.827(2)$ Å, $c = 6.753$-(3) Å, $V = 2929(1)$ Å^3, $Z = 4$, and $\rho_{\text{calcd}} = 1.63$ g cm^{-3}, but disorder

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prevented a satisfactory structure solution. The compound has no characteristic melting point. On heating in capillary it decomposes above 190 °C. TLC on SiO_2, $CHCl_3$:Me_2CO = 1:1: R_f = 0.56. IR data, cm^{-1}: 1667 m $\nu(C=N)$, 654 vs $\nu_3(SbF_6^-)$, 294 s, 286 s $\nu_4(SbF_6^-)$. ^1H NMR in CD_3OD, δ: the spectrum displays two groups of signals of equal intensities. Each group consists of four singlets: 2.172, 2.178, 2.186, 2.193 and 2.471, 2.477, 2.485, 2.492. ^1H NMR in CD_3OD/ CF_3CO_2H, δ: 2.29 (12 H), and 2.62 (12 H).

$[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$ and $[Pt(Me_2C=NO)_2$-$(Me_2C=NOH)_2]$. $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$ is prepared analogously to $[Pt(Me_2C=NO)(Me_2C=NOH)_3][SbF_6]$. Addition of 2 equiv of NaOH, instead of $NaSbF_6$, followed by slow evaporation of the solvent up to half the initial volume, results in release of $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$ as colorless prismatic crystals. The yield is 74%. Anal. Calcd for $C_{12}H_{30}N_4O_6Pt$: C, 27.64; H, 5.80; N, 10.74. Found: C, 27.89; H, 5.73; N, 11.01. IR data (Nujol), cm^{-1}: 3506 vs, 3412 vs $\nu(OH_2)$, 1649 m $\delta(OH_2)$, 1792 w, br $\nu(OH)$, 1622 m, 1603 s $\nu(C=N)$. A crystal for X-ray study was obtained directly from the reaction mixture. The powdered sample loses the crystallization water molecules, in a vacuum desiccator over silica, to give anhydrous $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]$. Anal. Calcd for the anhydrous sample, $C_{12}H_{26}N_4O_4Pt$: C, 29.69; H, 5.40; N, 11.54. Found: C, 29.60; H, 5.44; N, 11.47. EI-MS, m/z: 485 (M)$^+$. The compound has no characteristic melting point. On heating in a capillary, it decomposes above 225 °C. TLC on SiO_2, $CHCl_3$:Me_2CO = 2:1: R_f = 0.55. IR data, cm^{-1}: 1804 w, br $\nu(OH)$, 1621 m, 1600 s $\nu(C=N)$. ^1H NMR in acetone-d_6, δ: 2.04 (J_{PtH} = 10 Hz; 12 H), 2.19 (J_{PtH} = 10 Hz; 12 H).

$[Pt(Me_2C=NOH)_4]Cl_2$. Concentrated hydrochloric acid (*ca.* 35%, 3 mL) is added to a solution of $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]$ (0.20 g, 0.39 mmol) in water (2 mL) acidified by three drops of concentrated HCl. The precipitated $[Pt(Me_2C=NOH)_4]Cl_2$ is collected on a filter, washed twice with 1-mL portions of water, and dried in a vacuum desiccator over silica. The yield is 87%. Anal. Calcd for $C_{12}H_{28}Cl_2N_4O_4Pt$: C, 25.81; H, 5.05; N, 10.03. Found: C, 25.47; H, 5.15; N, 10.12. FAB$^+$-MS, m/z: 486 ($[Pt(Me_2C=NOH)_4] - H)^+$. When this compound is heated in the solid state at 165−180 °C, elimination of two 2-propanone oxime ligands and formation of *trans*-$[PtCl_2$-$(Me_2C=NOH)_2]$ are observed. Principal features of DTA/TG (heating rate 2 °C min^{-1}): 163 and 179 °C, endothermic peaks (mass loss 26.5%; calcd mass loss for elimination of two 2-propanone oxime ligands is 26.2%). IR data, cm^{-1}: 2854 s, 2810 s, 2753 s $\nu(OH)$, 1654 ms $\nu(C=N)$. ^1H NMR in DCl (20%)/D_2O, δ: 2.31 (12 H), 2.66 (12 H).

X-ray Structure Determination of *cis*-$[PtCl(Me_2C=NO)$-$(Me_2C=NOH)_2]$ and $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$. (Data for the latter compound are given in parentheses.) Diffraction data were collected on a Rigaku AFC7S diffractometer. Cell parameters and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 29.56° < 2θ < 29.96° (29.33° < 2θ < 30.01°); 9010 (2897) independent reflections [R_{int} = 0.040 (0.019)] were measured up to 60° by the $\omega-2\theta$ scan technique; 9457 (3092) reflections were collected. Range of *hkl*: *h* = 0 to 14, *k* = 0 to 23, *l* = −5 to 18 (*h* = 0 to 10, *k* = 0 to 18, *l* = −14 to 13). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standard intensities decreased by 1.8% (2.7%), and a linear correction for decay was applied. The data were corrected for Lorentz and polarization effects. An absorption correction using an empirical ψ scan method in the program TEXSAN[16] resulted in transmission factors ranging from 0.55 to 1.00 (0.60 to 1.00). All calculations and refinement were performed by using TEXSAN software.[16] The structures were solved and expanded by using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. H atoms were included at calculated positions but not refined for $[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$. (The H atoms corresponding to the water molecules in $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot$

Table 1. Crystal Data and Structure Refinement for $[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$ (**1**), $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$ (**2**), and $[Pt(Me_2C=NOH)_4]Cl_2$ (**3**)

	1	**2**	**3**
empirical formula	$C_9H_{20}ClN_3O_3Pt$	$C_{12}H_{30}N_4O_6Pt$	$C_{12}H_{28}Cl_2N_4O_4Pt$
fw	448.81	521.48	558.37
color; habit	colorless; prism	colorless; prism	colorless; cubic
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	10.533(2)	7.458(2)	9.922(2)
b, Å	17.075(4)	13.298(2)	12.205(2)
c, Å	17.131(2)	10.100(2)	17.241(3)
β, deg	102.79(1)	108.86(2)	100.35(3)
V, Å^3	3004.5(9)	947.9(3)	2053.9(6)
Z	8	2	4
ρ(calcd), g cm^{-3}	1.984	1.827	1.806
T, K	293 ± 1	293 ± 1	293 ± 2
radiation λ, Å	0.7107	0.7107	0.7107
μ, cm^{-1}	94.8	74.0	71.1
θ range, deg	2−30	2−30	2−25
no. of collcd reflcns	9457	3092	4150
no. of reflcns for calcns	5164	2897	2568
R^a	0.037	0.026	0.015 (R1^a)
R_w^b	0.043	0.037	0.037 (wR2^c)
goodness of fit	1.09	1.13	1.08

$^a R$ = R1 = $\sum ||F_o| - |F_c||/\sum |F_o|$. $^b R_w$ = $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. ^{c} wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

$2H_2O$ could not be located. All the other H atoms were found in a difference Fourier map, and their positions were refined with a fixed isotropic temperature factor.) Crystal size: 0.20 × 0.20 × 0.40 mm (0.30 × 0.30 × 0.20 mm). Scattering factors were taken from ref 18. Crystal data are given in Table 1, and bond distances and angles, in Tables 2 and 3.

X-ray Structure Determination of $[Pt(Me_2C=NOH)_4]Cl_2$. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Cell parameters were obtained from 12 centered reflections with θ between 10 and 12.5°; 4150 were collected, of which 2568 unique observed reflections (R_{int} = 0.040) with $I \geq 3\sigma(I)$ were measured up to 50° by the $\theta-2\theta$ scan technique. Range of *hkl*: *h* = 0 to 11, *k* = 0 to 14, *l* = −20 to 20. Diffractometer data were processed by the program PROFIT[19] with profile analysis of reflections. The structure was solved by means of a Fourier synthesis based upon the Pt atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[20] After that, all reflections with $I < 3\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least-squares procedures based on F^2 using the SHELX-93 package.[21] All non H atoms were treated anisotropically. Hydrogen coordinates were found from difference synthesis and refined isotropically. An extinction correction was applied. Lorentz, polarization, and absorption corrections were made.[22] Crystal size: 0.27 × 0.21 × 0.16 mm. T_{min} and T_{max} are 0.219 and 0.334, respectively. Scattering factors were taken from ref 18. Crystal data are given in Table 1, and bond distances and angles, in Table 4.

Results and Discussion

Syntheses of Building Elements for Crystal Engineering. The starting hypothesis for this work is that complexes of platinum(II) with 2-propanone oxime/oximato ligands should

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Table 2. Bond Lengths (Å) and Angles (deg) for [PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]

Pt(1)−Cl(1)	2.288(2)	Pt(1)−N(1)	1.993(7)
Pt(1)−N(2)	2.022(7)	Pt(1)−N(3)	2.032(7)
Pt(2)−Cl(2)	2.291(2)	Pt(2)−N(4)	1.992(7)
Pt(2)−N(5)	2.033(8)	Pt(2)−N(6)	2.029(7)
O(1)−N(1)	1.365(8)	O(2)−N(2)	1.406(9)
O(5)−N(5)	1.391(10)	O(3)−N(3)	1.396(9)
O(6)−N(6)	1.380(9)	O(4)−N(4)	1.368(8)
N(1)−C(1)	1.29(1)	N(2)−C(4)	1.30(1)
N(3)−C(7)	1.29(1)	N(4)−C(10)	1.29(1)
N(5)−C(13)	1.27(1)	N(6)−C(16)	1.30(1)
C(1)−C(2)	1.49(1)	C(1)−C(3)	1.49(1)
C(4)−C(5)	1.50(1)	C(4)−C(6)	1.46(1)
C(7)−C(8)	1.48(1)	C(7)−C(9)	1.51(1)
C(10)−C(11)	1.49(1)	C(10)−C(12)	1.49(1)
C(13)−C(14)	1.51(1)	C(13)−C(15)	1.49(1)
C(16)−C(17)	1.50(1)	C(16)−C(18)	1.48(1)
Cl(1)−Pt(1)−N(1)	90.6(2)	Pt(2)−N(4)−C(10)	129.1(6)
Cl(1)−Pt(1)−N(2)	176.6(2)	O(4)−N(4)−C(10)	117.7(7)
Cl(1)−Pt(1)−N(3)	90.7(2)	Pt(2)−N(5)−O(5)	115.7(5)
N(1)−Pt(1)−N(2)	87.0(3)	Pt(2)−N(5)−C(13)	126.8(7)
N(1)−Pt(1)−N(3)	176.3(3)	O(5)−N(5)−C(13)	116.2(8)
N(2)−Pt(1)−N(3)	91.8(3)	Pt(2)−N(6)−O(6)	117.2(5)
Cl(2)−Pt(2)−N(4)	89.8(2)	Pt(2)−N(6)−C(16)	128.4(7)
Cl(2)−Pt(2)−N(5)	175.2(2)	O(6)−N(6)−C(16)	114.4(7)
Cl(2)−Pt(2)−N(6)	91.0(2)	N(1)−C(1)−C(2)	121.0(8)
N(4)−Pt(2)−N(5)	85.4(3)	N(1)−C(1)−C(3)	121.7(8)
N(4)−Pt(2)−N(6)	177.8(3)	C(2)−C(1)−C(3)	117.2(8)
N(5)−Pt(2)−N(6)	93.8(3)	Pt(1)−N(1)−O(1)	113.7(5)
Pt(1)−N(1)−C(1)	129.3(6)	O(1)−N(1)−C(1)	116.8(7)
Pt(1)−N(2)−O(2)	115.3(5)	Pt(1)−N(2)−C(4)	130.1(7)
O(2)−N(2)−C(4)	114.3(7)	Pt(1)−N(3)−O(3)	117.6(5)
Pt(1)−N(3)−C(7)	128.7(7)	N(2)−C(4)−C(5)	121.6(9)
O(3)−N(3)−C(7)	113.4(8)	N(2)−C(4)−C(6)	119.0(9)
Pt(2)−N(4)−O(4)	112.9(5)	C(5)−C(4)−C(6)	119.3(9)
N(3)−C(7)−C(8)	123(1)	N(4)−C(10)−C(11)	122.2(8)
N(3)−C(7)−C(9)	119.2(9)	N(4)−C(10)−C(12)	119.4(8)
C(8)−C(7)−C(9)	117.3(10)	C(11)−C(10)−C(12)	118.4(8)
N(6)−C(16)−C(17)	119.8(10)	N(5)−C(13)−C(14)	121(1)
N(6)−C(16)−C(18)	120.5(9)	N(5)−C(13)−C(15)	120.5(9)
C(17)−C(16)−C(18)	119.7(10)	C(14)−C(13)−C(15)	118.3(9)

Table 3. Bond Lengths (Å) and Angles (deg) for [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O[a]

Pt(1)−N(1)	2.036(5)	Pt(1)−N(2)	2.023(4)
O(1)−N(1)	1.374(6)	O(2)−N(2)	1.361(6)
N(1)−C(1)	1.270(8)	N(2)−C(4)	1.285(7)
C(1)−C(2)	1.476(10)	C(1)−C(3)	1.493(9)
C(4)−C(5)	1.48(1)	C(4)−C(6)	1.484(9)
N(1)−Pt(1)−N(1)^a	180.0	N(1)−Pt(1)−N(2)	92.7(2)
N(1)−Pt(1)−N(2)^a	87.3(2)	Pt(1)−N(1)−C(1)	130.5(4)
Pt(1)−N(2)−O(2)	113.5(3)	O(2)−N(2)−C(4)	117.3(5)
N(1)−C(1)−C(3)	121.6(7)	N(2)−C(4)−C(5)	120.3(6)
C(5)−C(4)−C(6)	118.9(6)	N(2)−Pt(1)−N(2)^a	180.0
Pt(1)−N(1)−O(1)	112.4(4)	O(1)−N(1)−C(1)	117.0(5)
Pt(1)−N(2)−C(4)	128.9(4)	N(1)−C(1)−C(2)	120.3(6)
C(2)−C(1)−C(3)	118.0(7)	N(2)−C(4)−C(6)	120.8(6)

^{a} Symmetry operations used to generate equivalent atoms: 2 − x, −y, 2 − z.

Table 4. Bond Lengths (Å) and Angles (deg) for [Pt(Me$_2$C=NOH)$_4$]Cl$_2$

Pt−N(1)	2.014(4)	N(3)−C(8)	1.267(6)
Pt−N(3)	2.021(3)	N(4)−C(11)	1.277(5)
Pt−N(4)	2.022(3)	C(1)−C(2)	1.487(8)
Pt−N(2)	2.022(3)	C(2)−C(3)	1.488(8)
O(1)−N(1)	1.388(5)	C(4)−C(5)	1.470(7)
O(2)−N(2)	1.394(5)	C(5)−C(6)	1.489(6)
O(3)−N(3)	1.401(5)	C(7)−C(8)	1.474(9)
O(4)−N(4)	1.385(5)	C(8)−C(9)	1.500(7)
N(1)−C(2)	1.268(6)	C(10)−C(11)	1.479(7)
N(2)−C(5)	1.275(5)	C(11)−C(12)	1.480(7)
N(1)−Pt−N(3)	179.03(14)	C(11)−N(4)−O(4)	113.2(3)
N(1)−Pt−N(4)	86.75(14)	C(11)−N(4)−Pt	129.9(3)
N(3)−Pt−N(4)	93.22(14)	O(4)−N(4)−Pt	116.5(2)
N(1)−Pt−N(2)	93.46(14)	N(1)−C(2)−C(1)	120.8(5)
N(3)−Pt−N(2)	86.58(14)	N(1)−C(2)−C(3)	122.6(5)
N(4)−Pt−N(2)	179.30(13)	C(1)−C(2)−C(3)	116.5(6)
C(2)−N(1)−O(1)	111.9(4)	N(2)−C(5)−C(4)	121.1(4)
C(2)−N(1)−Pt	129.6(3)	N(2)−C(5)−C(6)	122.8(4)
O(1)−N(1)−Pt	117.7(3)	C(4)−C(5)−C(6)	116.1(4)
C(5)−N(2)−O(2)	113.1(3)	N(3)−C(8)−C(7)	120.8(5)
C(5)−N(2)−Pt	130.0(3)	N(3)−C(8)−C(9)	122.1(6)
O(2)−N(2)−Pt	116.6(2)	C(7)−C(8)−C(9)	117.1(6)
C(8)−N(3)−O(3)	112.0(4)	N(4)−C(11)−C(10)	119.8(4)
C(8)−N(3)−Pt	130.3(3)	N(4)−C(11)−C(12)	122.6(5)
O(3)−N(3)−Pt	116.9(3)	C(10)−C(11)−C(12)	117.5(5)

use this complex as a precursor for the stepwise preparative deprotonation leading to mixed oxime/oximato complexes of Pt(II). We wished to prepare in this way a complex with *cis* geometry and nonequivalent number of hydrogen-bond donor and acceptor sites, *i.e. cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]. This compound might be useful to analyze the formation and direction of intermolecular *vs* intramolecular hydrogen bonding. (ii) We wanted to prepare a complex with equivalent numbers of hydrogen bond donor and acceptor sites, *i.e.* [Pt(Me$_2$C=NO)$_2$-(Me$_2$C=NOH)$_2$]. This compound should be formally similar to metal *vic*-dioximes. Comparison of these two types of metal oximates would improve our understanding of the structural requirements for the formation of nonstacked or stacked complexes. Another interesting compound to disclose its hydrogen-bonding mode is [Pt(Me$_2$C=NOH)$_4$]Cl$_2$, *e.g.* the homoleptic dicationic complex which has four oxime ligands as potential H donors and chloride counterions as potential H acceptors.
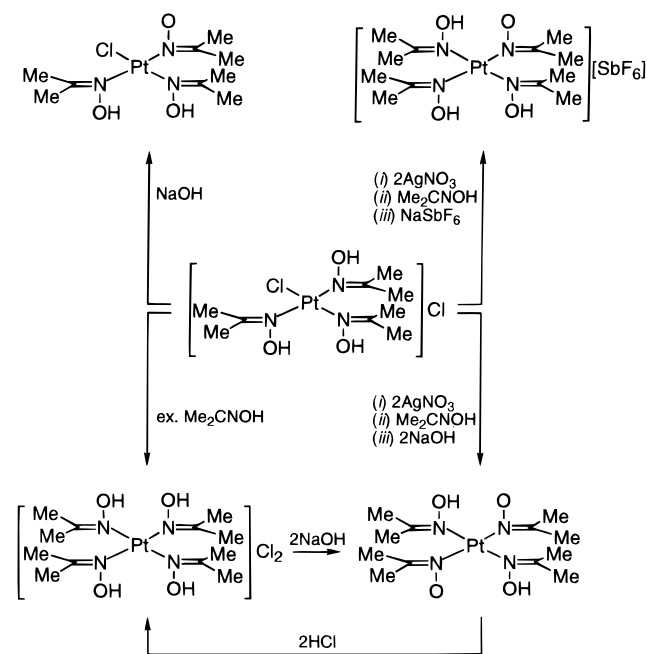
The complexes [PtCl(Me$_2$C=NOH)$_3$]Cl and [Pt(Me$_2$C=NOH)$_4$]-Cl$_2$ are known,[12,23,24] but neither detailed synthetic methods nor physicochemical properties (apart from pK_a values[12]) have been reported. We have developed synthetic procedures for the preparation of tris- and tetrakis(oxime/oximato) complexes of platinum(II) and report them in this paper (Scheme 1) along with elemental and X-ray analyses and FAB$^+$-MS, EI-MS, IR, and NMR data.

The cationic complex [PtCl(Me$_2$C=NOH)$_3$]Cl was synthesized by Babaeva and Mosyagina[23,24] by prolonged heating of *cis*-[PtCl$_2$(Me$_2$C=NOH)$_2$] with the oxime in acetone. We have observed that this compound can be easily obtained by heating *cis*-[PtCl$_2$(Me$_2$C=NOH)$_2$] in molten 2-propanone oxime; addition of a small amount of MeNO$_2$ to the reaction mixture decreases the melting point of the oxime and allows the synthesis to be carried out in the liquid phase.

The treatment of [PtCl(Me$_2$C=NOH)$_3$]Cl with 1 equiv of NaOH gives the neutral complex of *cis* geometry with one

have strong hydrogen bonds and also might have an increased tendency toward the formation of *inter*- rather than *intra*molecular hydrogen bonding. In that case, they could be used as building elements for designing complexes with extended arrays whose shapes and bonding structures are controlled by the geometrical configuration of the building elements and direction and number of hydrogen bonds. Therefore, our strategy for the preparation of suitable starting materials for the construction of polymeric oxime/oximato Pt(II) complexes held by hydrogen bonding was the following: (i) We wanted to synthesize a complex which contains neutral oxime ligands in the coordination sphere of platinum(II), *e.g.* [PtCl(Me$_2$C=NOH)$_3$]$^+$, and to

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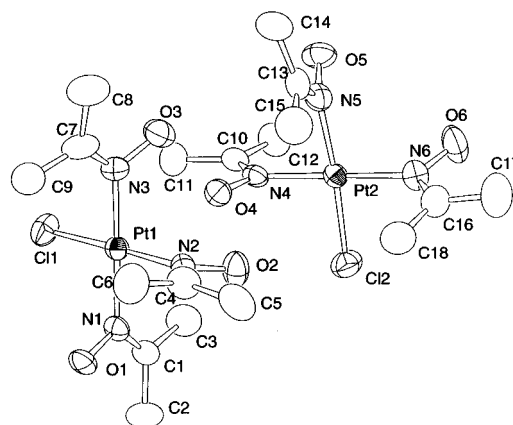**Scheme 1.** Studied Conversions of the Oxime Complexes

Figure 1. ORTEP plot of *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] with atomic numbering. Thermal ellipsoids are drawn at the 50% probability level.

oximato and two oxime ligands, *cis*-[PtCl(Me$_2$C=NO)-(Me$_2$C=NOH)$_2$], which was characterized by X-ray diffraction. Further, the reaction of [PtCl(Me$_2$C=NOH)$_3$]Cl with 2 equiv of AgNO$_3$ and successive addition of excess oxime and NaSbF$_6$ afford the chloride-free cationic complex [Pt(Me$_2$C=NO)-(Me$_2$C=NOH)$_3$](SbF$_6$), with one oximato and three oxime ligands. When a solution of NaOH, instead of NaSbF$_6$, was added to the reaction mixture, the neutral complex with two oximato and two oxime ligands, [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$], was formed. The latter product was isolated as the bis(hydrate) and structurally characterized. The infrared ν(OH$_2$) stretching frequencies (3506 and 3412 cm^{-1}) indicate that the crystallization water molecules are involved in weak hydrogen bonding.[25] The weakness of these hydrogen bonds accounts for the fact that, when powdered, [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O loses the two crystallization water molecules, to give anhydrous [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]. Both [Pt(Me$_2$C=NO)$_2$-(Me$_2$C=NOH)$_2$] and [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O show a weak broad band around 1800 cm^{-1} that can be assigned to the O−H stretching frequency of the intramolecular hydrogen-bridged −O$^-$···HO− bond in oxime/oximato complexes.[26]

Although Cl$^-$ ligands in [PtClL$_3$]$^+$ complexes (L is, *e.g.*, NH$_3$ or pyridine[27]) are easily substituted by L, displacement of coordinated Cl$^-$ in [PtCl(Me$_2$C=NOH)$_3$]Cl by Me$_2$C=NOH proceeds slowly even on refluxing in the presence of a 20-fold excess of the oxime in nitromethane. After 10 h, the conversion of [PtCl(Me$_2$C=NOH)$_3$]Cl to [Pt(Me$_2$C=NOH)$_4$]Cl$_2$ does not exceed 5−10% as observed by ^{1}H NMR monitoring. Despite low conversion, slow evaporation of nitromethane from the reaction mixture gave some X-ray-quality crystals of [Pt-(Me$_2$C=NOH)$_4$]Cl$_2$. This homoleptic complex was also prepared according to the published method[24] by addition of excess HCl to [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]. In turn, addition of 2 equiv of NaOH to [Pt(Me$_2$C=NOH)$_4$]Cl$_2$ regenerates [Pt-(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$].

We have characterized the thermal properties of [PtCl-(Me$_2$C=NOH)$_3$]Cl and [Pt(Me$_2$C=NOH)$_4$]Cl$_2$. These com-

pounds are relatively stable at room temperature both in aqueous solutions and in the solid state. When they were heated in the solid phase, elimination of one (former case) or two (latter case) oxime molecules was observed in a DTA/TG study (see Experimental Section). In both cases, the formation of *trans*-[PtCl$_2$(Me$_2$C=NOH)$_2$] was verified by preparative experiments. It is worthwhile to mention that, although solid-state thermal displacement of the oxime ligands had not yet been reported, a few examples of elimination of some other N-donor ligands from platinum(II) complexes are documented.[28]

Structure of *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]: Self-Assembly by Hydrogen Bonding. The complex *cis*-[PtCl-(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] contains two crystallographically independent molecules in the solid state. In each of these molecules, three N atoms and one Cl atom form a slightly distorted square-planar coordination sphere around the Pt atom (Figure 1).

All 2-propanone oxime/oximato ligands are planar and coordinated through their nitrogen atoms. Although hydrogen atoms could not be located, it is clear from the molecular geometry (see below) that O(1) and O(4) atoms correspond to oximato ligands while the other oxygen atoms [O(2), O(3), (O5), and O(6)] correspond to neutral oxime ligands, thus providing the *cis* geometry of [PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]. The arrangement of the oxime ligands is such that the oxygen atoms O(5) and O(6) [O(2) and O(3)] are situated above the coordination plane, while O(1) [O(4)] for the oximato ligand is below the plane. The oximato oxygen atoms are intermolecularly hydrogen bonded in a chelate-like way by two OH groups of the oxime ligands from a neighboring molecule. The distances O(4)···O(2) and O(4)···O(3) are 2.576(9) and 2.522(9) Å, respectively, while O(1)···O(5) and O(1)···O(6) are 2.527(8) and 2.500(9) Å, correspondingly. As expected for negative charge assisted hydrogen bonding,[11] these distances are in the range of strong hydrogen bonds, in agreement with the appearance of ν(OH) at 1676 cm^{-1} in the IR spectrum.[29]

Two crystallographically independent molecules of *cis*-[PtCl-(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] form the repeat unit for the infinite

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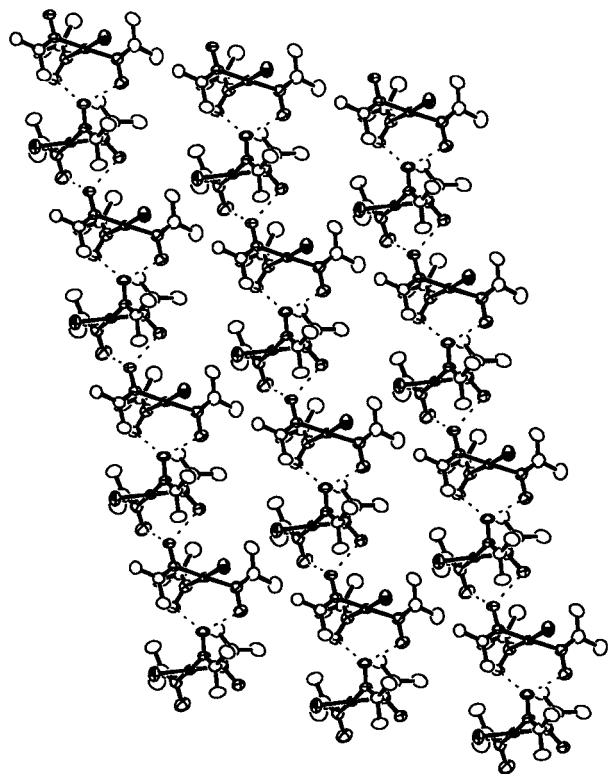(29) Novak, A. *Struct. Bonding (Berlin)* **1974**, *18*, 177.

Figure 2. Molecular packing diagram of *cis*-[PtCl(Me$_2$C=NO)-(Me$_2$C=NOH)$_2$].

one-dimensional polymeric chains held by H-bonds (Figure 2). Thus, the *cis* geometry of the complex as the building element with one oximato and two oxime species plays an important role in determining the shape and bonding structure of this extended array.

The fact that the OH groups are involved in inter- rather than intramolecular hydrogen bonds leads to long intramolecular O···O distances [O(2)···O(3) 3.74(1) and O(5)···O(6) 3.87(1) Å].

The hydrogen-bond rules for organic compounds state that six-membered-ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds and that the best proton donors and acceptors remaining after intramolecular hydrogen-bond formation form intermolecular hydrogen bonds to another.[2] Nevertheless, *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] does not form an intramolecular hydrogen bond between an oxime and an oximato ligand (as in the case of [Pt(Me$_2$C=NO)$_2$-(Me$_2$C=NOH)$_2$]·2H$_2$O; see below); but on contrary, it forms only intermolecular hydrogen bonds.

It is also worthwhile to discuss the structural characteristics of the building element, *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]. The negative charges on the oximato ligands make them better donors, and the Pt−N(oximato) distances [1.993(7) and 1.992-(7) Å] are shorter than the Pt−N(oxime) distances [2.022(7)−2.033(8), average 2.029 Å; see Table 2]. Indeed, the Pt−N(oxime) distances are very close to those found in [Pt(Me$_2$C=NOH)$_4$]Cl$_2$ [2.014(4)−2.022(3) Å; see below]. The loss of a proton on going from oxime to oximato ligands should also affect the ligand geometry. Thus, *ab initio* molecular orbital calculations indicate that deprotonation of the OH group in CH$_2$=C(H)OH leads to a shortening of the C−O bond and a lengthening of the C=C bond.[30] If we assume a similar behavior for coordinated oximes, we would expect that deprotonation would shorten the N−O distance and increase the C=N

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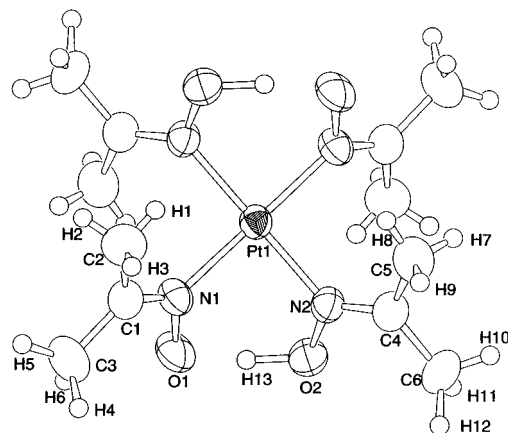
**Figure 3.** ORTEP plot of the centrosymmetric [Pt(Me$_2$C=NO)$_2$-(Me$_2$C=NOH)$_2$] molecule in [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O with atomic numbering. Thermal ellipsoids are drawn at the 50% probability level.

bond length. The structure of [PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] contains both oxime and oximato ligands, and the N−O (oximato) distances [1.365(8) and 1.368(8) Å, average 1.367-(8) Å] are shorter than the N−O(oxime) distances [1.380(9)−1.406(9) Å, average 1.393(9) Å; see Table 2], although the difference is not significant. The average N−O(oxime) distance in [Pt(Me$_2$C=NOH)$_4$]Cl$_2$ is 1.392(6) Å (see below). The prediction that the C=N bond should be longer for oximato than for oxime ligands cannot be confirmed because of the relatively high standard deviations. Nevertheless, the infrared spectrum of *cis*-[PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$] shows bands at 1544 and 1537 cm^{-1} that can be assigned to ν(C=N) of the oximato ligands, while a weak band at 1614 cm^{-1} probably corresponds to ν(C=N) of the neutral oxime ligands. These values point to stronger C=N bonds for oxime than for oximato ligands. In both crystallographically independent molecules, the dihedral angles between the Me$_2$C=NO planes and the coordination plane are in the ranges 74−84° for oxime and 88−90° for oximato ligands.

Structure of [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O: Formation of a Two-Dimensional Network. In the [Pt-(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O complex, the Pt atom lies on an inversion center and four N atoms form a slightly distorted square-planar coordination sphere around the Pt atom (Figure 3).

All the ligands are planar and bonded to the Pt atom through their nitrogen atoms. The oxime and oximato ligands form six-membered rings involving very strong intramolecular hydrogen bonds [O(1)···O(2) 2.445(6) Å].

Bearing in mind that very strong O−H···O hydrogen bonds *tend* to be symmetric,[11] we would expect that ligands should have mixed oxime/oximato character. In agreement with this expectation, and in contrast to the structure of [PtCl(Me$_2$C=NO)-(Me$_2$C=NOH)$_2$], there are no notable geometrical differences between oxime and oximato ligands (see Table 3). For this reason, no infrared bands below 1550 cm^{-1} can be assigned to ν(C=N) of the oximato ligands (*cf.* 1544 and 1537 cm^{-1} for [PtCl(Me$_2$C=NO)(Me$_2$C=NOH)$_2$]). Nevertheless, the complex [Pt(Me$_2$C=NO)$_2$(Me$_2$C=NOH)$_2$]·2H$_2$O shows two ν(C=N) vibrations at 1622 and 1603 cm^{-1}, which suggests that the two sets of ligands have unequal contribution of oximato and oxime ligand character and, indeed, the intramolecular hydrogen bond is not symmetric [O(2)−H(13) 1.01(7) Å; H(13)···O(1) 1.52-(7) Å; O(2)−H(13)···O(1) 150(6)°]. Eventually, the building elements containing intramolecular hydrogen bonds are connected by intermolecular hydrogen bonds with two crystalliza-
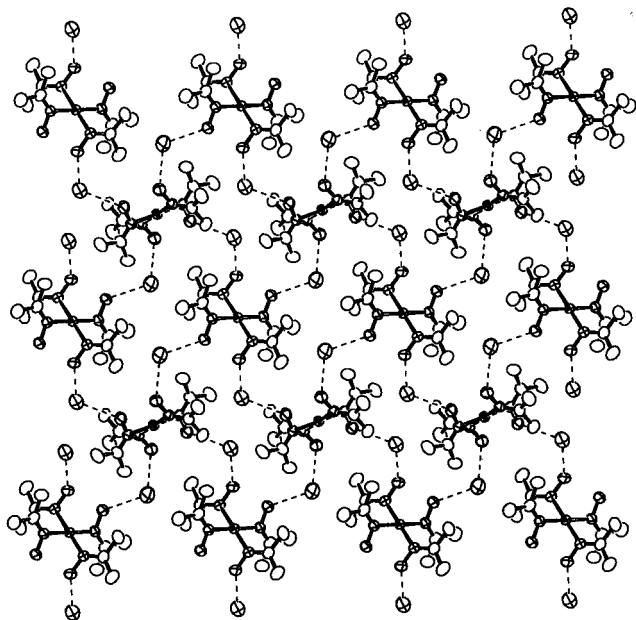
Figure 4. Molecular packing diagram of $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$.

tion water molecules [O(1)···O(3) 2.879(8) Å; O(2)···O(3) 2.775(8) Å] to form a layered two-dimensional network (Figure 4).

For the formation of this network, the conformation of all four ligands around the Pt(II) center—which is controlled by two strong intramolecular hydrogen bonds—and the hydrogen bonding ability of the four O atoms of the ligands with H_2O molecules are important factors. The similarity between the IR spectra of $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$ and $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]$, and the weakness of the intermolecular hydrogen bonds with H_2O in $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$, which allows easy dehydration, suggest that the anhydrous material also has similar intramolecular hydrogen bonding.

In contrast to those of *cis*-$[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$ (see above) and $[Pt(Me_2C=NOH)_4]Cl_2$ (see below), the ligand planes are strongly twisted relative to the coordination plane. The dihedral angles between the $Me_2C=NO$ planes and the coordination plane are 51.36 and 53.26° as a result of the compromise between shortening the O(1)···O(2) distance and reducing the steric hindrance between the methyl groups.

It is interesting to note that while *vic*-dioxime complexes of Ni(II) have short intramolecular O—H···O hydrogen bonds, the O···O distances increase on going from Ni(II) to Pd(II) and Pt(II) complexes, probably due to the increase in M—N distance.[13] Furthermore, the bidentate bite angle for *vic*-dioximes coordinated to Pt(II) is about 80°, thus forcing the N—Pt—N angle in the hydrogen-bonded PtNOH···ON ring to open up from 90° to about 100°[31] and preventing the oxygen atoms from being closer. Therefore, the intramolecular hydrogen bonds in *vic*-dioxime Pt(II) complexes cannot be very short. Indeed, O···O distances in the range 2.65—3.03 Å have been reported for this kind of compounds.[31] On the other hand, in Pt(II) complexes with *simple* oxime and oximato ligands, such as $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$, the N—Pt—N angle in the hydrogen-bonded PtNOH···ON ring is smaller than 90°

[87.3(2)°] to allow a closer approach of the hydrogen-bonded oxygen atoms [O(1)···O(2) 2.445(6) Å]. Therefore, it is clear that $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$ has a stronger intramolecular hydrogen bond than Pt(II) complexes with *vic*-dioximes.

Structure of the Caged Complex $[Pt(Me_2C=NOH)_4]Cl_2$. In the homoleptic $[Pt(Me_2C=NOH)_4]Cl_2$ compound, four N atoms form a slightly distorted square-planar coordination sphere around the Pt atom as shown in Figure 5.

All 2-propanone oxime ligands are planar and bonded to the Pt atom through their nitrogen atoms. The distances of the bonds Pt—N [2.014(4)—2.022(3) Å], N—O [1.385(5)—1.401(5) Å], and N—C [1.267(6)—1.277(5) Å] are normal. The dihedral angles between the $Me_2C=NO$ planes and the coordination plane are in the range of 83—90°, and the arrangement of the ligands is such that the oxygen atoms O(1) and O(2) from two of the 2-propanone oxime ligands are situated above the PtN(1)N(2)N(3)N(4) plane, whereas O(3) and O(4) from the other two ligands are below the plane. Both Cl^- counterions are hydrogen bonded (in a chelate-like way similar to that found in *cis*-$[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$) by two OH groups of the 2-propanone oximes, with O···Cl^- distances in the range 2.92—2.97 Å. According to Wells,[32] distances within the range 2.95—3.4 Å are found for O—H···Cl^- hydrogen bonds (for Cl^-···H_3O^+ the distance is 2.95 Å[32]). Therefore, the H-bonds in $[Pt(Me_2C=NOH)_4]Cl_2$ are among the shortest O—H···Cl^- hydrogen bonds reported, although a shorter bond (2.89 Å) was reported recently.[33] The infrared spectrum also agrees with the existence of strong O—H···Cl^- hydrogen bonds, because the appearance of ν(OH) at 2854, 2810, and 2753 cm^{-1}, indicates O···Cl^- distances well below 3 Å.[25,34]

The structure of $[Pt(Me_2C=NOH)_4]Cl_2$ is in some respects similar to that reported previously for dichlorotetrakis(acetal-doxime)nickel(II).[35] A significant difference, however, between both structures is that, although in the nickel complex the Cl atoms are coordinated to the metal atom [Ni—Cl, 2.441(1) Å], giving rise to an octahedral structure, in the platinum complex the Cl^- ions are not coordinated to the platinum atom but held only by hydrogen bonds. The lack of coordination is demonstrated not only because the Pt···Cl distances [Pt···Cl(1) 3.794(2) and Pt···Cl(2) 3.792(2) Å] are longer than the sum of

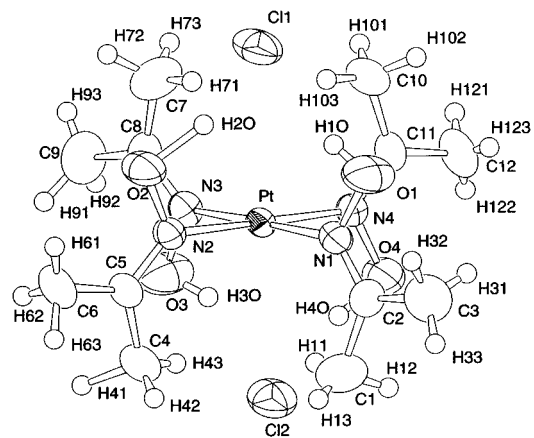**Figure 5.** ORTEP plot of $[Pt(Me_2C=NOH)_4]Cl_2$ with atomic numbering. Thermal ellipsoids are drawn at the 50% probability level.

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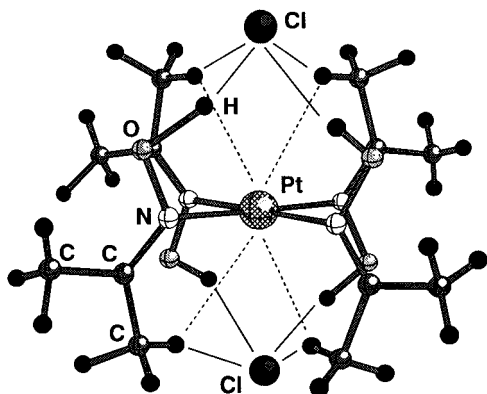
Figure 6. Ball and Stick view of $[Pt(Me_2C=NOH)_4]Cl_2$ indicating hydrogen bonds with Cl^- (solid lines) and $H\cdots Pt$ interactions (dashed lines).

van der Waals radii $[Pt(1.75) + Cl(1.75) = 3.50 \text{ Å}^{36}]$ but also because the $N-Pt\cdots Cl$ angles deviate significantly from $90°$ (average deviation *ca.* 17°) while in the nickel complex the maximum deviation was 1.5°.[35] In agreement with the lack of $Pt-Cl$ bonds, the infrared spectrum shows the disappearance of the $\nu(Pt-Cl)$ band at 342 cm^{-1} on going from $[PtCl(Me_2C=NOH)_3]Cl$ to $[Pt(Me_2C=NOH)_4]Cl_2$.

A further analysis of the structure of $[Pt(Me_2C=NOH)_4]Cl_2$ revealed the presence of other short contact distances between one hydrogen atom from every CH_3 group *cis* to the platinum atom and both the Cl^- counterion and the Pt atom, Figure 6.

Although X-ray diffraction experiments may allow the location of the hydrogen atom's *electron cloud* with limited accuracy, neutron diffraction determines accurately the position of the hydrogen atom's nucleus.[37] For that reason, $C-H$ distances determined by X-ray diffraction are systematically shorter than those determined by neutron diffraction, and an analysis of the hydrogen bond geometry is best done after correction of H atom positions to neutron normalized values with $C-H$ distances of 1.08 Å.[38a] After these corrections, the four $H\cdots Cl$ and $H\cdots Pt$ contact distances are in the ranges 2.72–2.79 and 2.67–2.81 Å, respectively. All the normalized distances are shorter than the sum of van der Waals radii [2.95 Å for both $H\cdots Cl$ and $H\cdots Pt^{36}$]. The angles $C-H\cdots Cl$ and $C-H\cdots Pt$ are in the ranges 151–162° and 110–120°, respectively. Although less studied than $C-H\cdots O$ hydrogen bonds,[38,39] $C-H\cdots Cl$ hydrogen bonds are relatively well-documented.[8b,39–41] While a short intermolecular $C-H\cdots Cl$ hydrogen bond has been reported for $[PtCl\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}(C\equiv CH)\text{-}4\}]$,[8b] Taylor and Kennard[39] noted a tendency for $(C-)H$ atoms to form short contacts of the type $(C-)H\cdots Cl^-$ rather than $(C-)H\cdots Cl-R$, and this indication gives a favorable argument for the existence of $C-H\cdots Cl$ hydrogen bonds in $[Pt(Me_2C=NOH)_4]Cl_2$. Another important factor in the formation of $C-H\cdots X$ hydrogen bonds is the acidity of the $C-H$ groups,[38b] and $C-H\cdots Cl^-$ hydrogen bonds in $[Pt(Me_2C=NOH)_4]Cl_2$ are not expected to be strong. In the related compound dichlorotetrakis(acetaldoxime)nickel(II),[35] $H\cdots Cl$ distances of 2.65–2.67 Å for the $(N=C)-H$ hydrogen atoms are indicative of hydrogen bonds

although the authors[35] did not mention the $H\cdots Cl$ hydrogen bonding. Of course, these hydrogens are more acidic than the methyl hydrogens in $[Pt(Me_2C=NOH)_4]Cl_2$.

Unless short $(C-)H\cdots Pt$ distances are the fortuitous result of other interactions, their origin can be assigned to either three-center two-electron (agostic)[42] or three-center four-electron (hydrogen-bonding)[43] interactions. Whereas in the former interactions the metal atom accepts electron density from the $C-H$ bond, in the latter interactions the electron-rich transition metal acts as hydrogen-bond acceptor. Therefore, the electron-rich Pt(II) is more likely to be involved in hydrogen-bond-like interactions. Indeed, hydrogen bonding with transition metal centers was briefly reviewed recently,[43,44] and several Pt(II) complexes display $C-H\cdots Pt$ or $N-H\cdots Pt$ interactions of this type.[40,45] Also, $O-H\cdots Pt$ hydrogen bonds have been reported.[46,47] Crabtree and co-workers have reviewed the geometrical features of $N-H\cdots M$ and $C-H\cdots M$ interactions in d^8 square planar complexes.[48] They concluded that the $N-H\cdots M$ interactions are best regarded as hydrogen bonds, but the nature of the $C-H\cdots M$ interactions remains unclear, although a weak hydrogen bond is perhaps involved.[48] On the other hand, Braga *et al.* consider that short $(C)H\cdots M$ separations associated with large $C-H\cdots M$ angles $(>100°)$ most likely correspond to $C-H\cdots M$ hydrogen bonds.[44]

Although there seems to be almost no doubt about the presence of strong $O-H\cdots Cl^-$ hydrogen bonds in $[Pt(Me_2C=NOH)_4]Cl_2$, we may wonder whether the relatively short $(C-)H\cdots Cl$ and $(C-)H\cdots Pt$ contact distances are the result of attractive interactions involving the methyl hydrogen atoms or just the fortuitous result of other interactions. Thus, the geometry of the oxime ligand forces the $Pt\cdots C(\textit{cis}\text{-methyl})$ distances to be around 3.34 Å. Furthermore, the $O-H\cdots Cl^-$ hydrogen bonds may be responsible for the orientation of the ligands, thus determining the position of all the non-hydrogen atoms of the oxime ligand and forcing the methyl groups to approach the other Cl^- ion. Bearing in mind that there may be free rotation around the $C-CH_3$ bond, the question is whether one H atom is looking for the Cl^- ion, for the Pt atom, for both or, on the contrary, is trying to avoid both of them. The results of molecular modeling by use of the ChemDraw 3D program indicate that, in order to minimize the $H\cdots Pt$ distances, the methyl groups should be rotated in the direction opposite to that which minimizes the $H\cdots Cl$ distances. Indeed, the experimentally determined positions are quite close to those that minimize the sum of the $H\cdots Pt$ and $H\cdots Cl$ distances. Taking into account that a rotation of about 60° would be necessary to keep the methyl hydrogens as far apart as possible from the Pt

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and Cl atoms, we believe that the $(C-)H\cdots Pt$ and $(C-)H\cdots Cl$ interactions, although weak, are real attractive interactions that could be considered to give rise to bifurcated hydrogen bonds as indicated in Figure 6. To the best of our knowledge, this kind of interaction had not been reported previously, although it is similar to the so-called "intermolecular multicenter heteroacceptor (IMH) hydrogen bond".[44] In our case, however, the $(C-)H\cdots Pt$ interaction is intramolecular and the electronegative atom (Cl) is not coordinated to the Pt atom. In any case, the modeling suggests that the molecules always pack in such a way to minimize the total energy, and to obtain this, the number of weak dipolar attractive interactions is maximized. Admittedly, these conclusions are based only on the positions of hydrogen atoms that are determined with low accuracy by X-ray diffraction, and it would be desirable to obtain neutron diffraction data on this compound. Also, we are currently involved in the preparation of $[Pt(Me_2C=NOH)_4]X_2$ complexes with different counterions X^- in order to investigate their structural features.

Desiraju[38a] has pointed out that crystal structures cannot be rationalized from consideration of strong hydrogen bonding alone and that all possible interactions of a molecule must be taken into account. For that reason, the Cl^- counterions may be considered to be involved in unusual $(\mu_4\text{-}Cl^-)\cdot cis\text{-}[(\cdots H-O-)_2(\cdots H-CH_2-)_2]$ hydrogen bonding; *i.e.*, they are situated at the vertex of an irregular square pyramid with a basal plane formed by two hydrogens from the OH and two hydrogens from the CH_3 groups, thus forming a caged complex, Figure 6. It is worthwhile to mention that Stone *et al.*[35] indicated only hydrogen bonding between the OH groups of aldoximes and Cl atoms in the structure of dichlorotetrakis(acetaldoxime)-nickel(II). However, the distances between hydrogens of the $-C(H)=$ groups and the Cl ligands (2.65 and 2.67 Å) indicate a similar $(\mu_4\text{-}Cl)\cdot cis\text{-}[(\cdots H-O-)_2(\cdots H-C)_2]$ hydrogen bonding in $[NiCl_2(MeCH=NOH)_4]$. Although the methyl hydrogens in $[Pt(Me_2C=NOH)_4]Cl_2$ are not acidic enough to be involved in strong hydrogen bonds, perhaps the soft character of the methyl groups enhances the interaction with the soft Cl and Pt centers.[38a,49] Nevertheless, it should be pointed out that Cotton *et al.* recently called for caution against the relaxed definitions that do not distinguish between a hydrogen bond and a classical van der Waals interaction.[50]

Concluding Remarks

Several conclusions can be drawn from this study. (i) The structural features of the platinum complexes with 2-propanone oxime are in a number of significant aspects different from those for complexes with *vic*-dioxime ligands. While *vic*-dioxime complexes are characterized by deprotonation of one oxime OH group and formation of intramolecular hydrogen bonds, the flexibility of 2-propanone oxime/oximato species around the Pt−N bond allows the formation of intermolecular $-O^-\cdots HO-$ hydrogen bonds, hydrogen bonds with counterion, $(\mu_4\text{-}Cl^-)\cdot cis\text{-}[(\cdots H-O-)_2(\cdots H-CH_2-)_2]$, and $Pt\cdots H-CH_2-$ interactions. Further, the intramolecular hydrogen bonds are stronger for platinum complexes with 2-propanone oxime/oximato ligands than for those with *vic*-dioxime species because of the loss of the strain in the five-membered PtNCCN ring in the *vic*-dioxime

chelates. In addition, the steric hindrance due to the bulky $=CMe_2$ moieties prevents these polymeric structures from stacking and gives rise to long $Pt\cdots Pt$ separations. Thus, in $[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$ the closest $Pt\cdots Pt$ distance between chains is 7.83 Å, while in $[Pt(Me_2C=NO)_2\text{-}(Me_2C=NOH)_2]\cdot 2H_2O$ all layers have a $Pt\cdots Pt$ separation of 7.46 Å. In contrast, in *vic*-dioxime Pt(II) complexes, the flat complex units are stacked one on top of the other, giving rise to columnar structures with $Pt\cdots Pt$ distances in the range 3.17−3.50 Å.[31]

(ii) The empirical hydrogen-bond rules for organic compounds state that (a) all good proton donors and acceptors are used in hydrogen bonding, (b) six-membered-ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds, and (c) the best proton donors and acceptors remaining after intramolecular hydrogen-bond formation form intermolecular hydrogen bonds to another.[2] Coordinated neutral oximes are good proton donors[9] and coordinated oximato groups are good proton acceptors. Therefore, in $[Pt(Me_2C=NO)_2\text{-}(Me_2C=NOH)_2]\cdot 2H_2O$, oxime and oximato groups form six-membered-ring intramolecular hydrogen bonds, while the water molecules form weak intermolecular hydrogen bonds with oxime/oximato groups. The expected trend, however, is not followed by $[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$, which forms *inter*- rather than *intra*molecular hydrogen bonds. Apparently the adopted structures of $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$ and $[PtCl(Me_2C=NO)(Me_2C=NOH)_2]$ are the result of optimizing the number and strength of hydrogen bonds. The strongest hydrogen bond is intramolecular, and it is formed for $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2]\cdot 2H_2O$, where there are the same number of donor and acceptor sites, *e.g.* two OH groups and two negatively charged O atoms. For $[PtCl(Me_2C=NO)\text{-}(Me_2C=NOH)_2]$, there are two H-donor sites and one H-acceptor site, *i.e.* two OH groups and only one negatively charged O atom. Therefore, the compromise between number and strength of hydrogen bonds gives rise to two strong intermolecular H-bonds rather than only one very strong intramolecular H-bond. This remarkable behavior points to the need for a better understanding of the factors affecting the preference of inter-*vs* intramolecular hydrogen bonding in oxime/oximato Pt(II) complexes.

The present study points to a rich structural chemistry of oxime/oximato Pt(II) complexes that could be useful for crystal engineering. Nevertheless, more studies are necessary to confirm this potential use.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**−**3** are available on the Internet only. Access information is given on any current masthead page.

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