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Pt(IV)-Mediated Redox Coupling of 2-Propanone Oximes in *cis*-[$Pt(Me_2C{=}NOH)_2Cl_4$]. Crystal Structure of [$Pt(N({=}O)CMe_2ONCMe_2)Cl_2$]

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The complex *cis*-[$Pt(Me_2C{=}NOH)_2Cl_2$], **1**, isomerizes into *trans*-[$Pt(Me_2C{=}NOH)_2Cl_2$], **2**, upon heating in the solid phase at 140 °C. Isomerization of **1** into **2** was also performed in acetonitrile or acetone solutions, containing catalytic amounts of $Me_2C{=}NOH$; in the DMF–DMSO mixture, a 2-propanone oxime is displaced by DMSO in formation of *cis*-, **3**, and *trans*-[$Pt(Me_2C{=}NOH)(DMSO)Cl_2$], **4**. An excess of dimethyl sulfoxide results in the formation of the well-known complex *cis*-[$Pt(DMSO)_2Cl_2$]. Complex **4** has also been obtained from K[$Pt(DMSO)Cl_3$] and $Me_2C{=}NOH$ in water, and complex **3** results from the solid-phase thermal isomerization of **4**. The oxidation of **1** and **2** by molecular chlorine in $CHCl_3$ or in $MeNO_2$ produces *cis*-, **5**, and *trans*-[$Pt(Me_2C{=}NOH)_2Cl_4$], **6**. Complex **6** is relatively stable in a water–acetone mixture, but complex **5** in this mixture at 20–25 °C is converted within 3 h into a product containing an unusual redox coupling of 2-propanone oximes, [$Pt(N({=}O)CMe_2ONCMe_2)Cl_2$], **7**. All the complexes were characterized by elemental analysis, IR spectra, and ^1H, ^{13}C, and ^{195}Pt NMR spectra; X-ray structure analysis was performed for **7**. The compound crystallizes in the orthorhombic space group $Pn2_1a$. The unit cell dimensions are $a = 8.860$ (3), $b = 8.022$ (2), $c = 15.744$ (4) Å, $V = 1119.0$ (6) Å^3, $Z = 4$, and $\rho_{calcd} = 2.43$ g cm^{-1}. Complex **1** is decomposed under X-ray irradiation, but crystallographic parameters have been determined (monoclinic, space group $B2/b$, $a = 11.074$ (3), $b = 16.114$ (4), $c = 8.177$ (1) Å, $\gamma = 111.76$ (1)°, $V = 1355.0$ (5) Å^3, $Z = 4$).

Introduction

The reaction of metal-bound organonitriles with water is known to result in the formation of coordinated carboxamides[1] without further hydrolysis in the formation of ammine complexes and RCO_2H. However, it has been established[2] that the RCN (R = Me, Ph) molecules in the Pt(IV) complexes hydrolyze completely even on exposure of the solid samples to open air at room temperature. This leads to a mixture of products, among which ammine complexes of Pt and RCO_2H have been isolated and identified. The complete hydrolysis of coordinated organonitriles was suggested to be due to an extremely strong electrophilic activation of the RCN molecules by a quadruple-charged Pt ion (a so-called Lewis superacid[1d]).

Such an important change in reactivity of organonitriles in the Pt(IV) complexes, as compared to that of free RCN ligands, or to that of organonitriles in Pt(II) complexes,[3] prompted us to study the Pt(IV) compounds with other ligands having the C—N bond. Our preliminary results imply that PhCH=NMe and PhCH=NPh ligands in the Pt(IV) complexes are much more susceptible to hydrolysis than in the respective Pt(II) complexes. For this study we address derivatives of Pt(IV) with 2-propanone oxime.

The chemistry of Pt complexes with oximes is less known than that with other N-donor ligands of the sp^2 type.[1b,4,5] Oximes coordinated to platinum are known to be subject to fairly easy deprotonation, either preserving the Pt—N bond[6] or leading to formation of Pt—O—N oximato compounds.[7] The $R_2C{=}NOH$ ligands in other metal complexes undergo deprotonation accompanied by formation of oximato $\overline{[\mathrm{M}]\text{—O—}\mathrm{N}}$[8a,b] and bridging oximato μ_2-η^2-$ONCR_2$[8c,d] complexes. Other reactions are the Beckman rearrangement,[9] deoxygenation,[10] dehydration with

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(1) (a) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977,** *23,* 1. (b) Kukushkin, Yu. N. *Reactivity of Coordination Compounds*; Khimia: Leningrad, 1987; p 151. (c) Zilberman, E. N. *Uspekhi Khim.* **1984,** *53,* 1548. (d) Paul, P.; Nag, K. *Inorg. Chem.* **1987,** *26,* 1586.

(2) (a) Kukushkin, V. Yu.; Zenkevich, I. G.; Belsky, V. K.; Konovalov, V. E.; Moiseev, A. I.; Sidorov, E. O. *Inorg. Chim. Acta* **1989,** *166,* 79. (b) Kukushkin, V. Yu.; Belsky, V. K.; Moiseev, A. I.; Konovalov, V. E. *Zh. Obsch. Khim.* **1989,** *59,* 1449.

(3) Rochon, F. D.; Kong, P. C.; Melanson, R. *Inorg. Chem.* **1990,** *29,* 1352.

(4) For a brief general review concerning oxime and oximato complexes, see: Mehrotra, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, pp 269–270.

(5) Kukushkin, Yu. N. *The Chemistry of the Coordination Compounds*; Vyshaya Shkola: Moscow, 1985; see also references therein.

(6) (a) Grinberg, A. A.; Stetsenko, A. I.; Strelin, S. G. *Zh. Neorg. Khim.* **1968,** *13,* 1089. (b) Stetsenko, A. I.; Strelin, S. G.; Gelfman, M. I. *Zh. Neorg. Khim.* **1970,** *15,* 134. (c) Stetsenko, A. I.; Skvortsov, N. K.; Lipner, B. S. *Zh. Obsch. Khim.* **1975,** *45,* 1783. (d) Kukushkin, Yu. N.; Stetsenko, A. I.; Duibanova, V. G.; Strelin, S. G. *Zh. Neorg. Khim.* **1974,** *19,* 2497. (e) Kukushkin, Yu. N.; Stetsenko, A. I.; Duibanova, V. G.; Strelin, S. G. *Zh. Neorg. Khim.* **1971,** *16,* 3078. (f) Stetsenko, A. I.; Lipner, B. S. *Zh. Obsch. Khim.* **1974,** *44,* 2289. (g) Kukushkin, Yu. N.; Stetsenko, A. I.; Strelin, S. G.; Duibanova, V. G. *Zh. Neorg. Khim.* **1972,** *17,* 1083.

(7) Babaeva, A. B.; Mosyagina, M. A. *Dokl. Akad. Nauk SSSR* **1953,** *89,* 293.

(8) (a) Beirakhov, A. G.; Orlova, I. M.; Ashurov, Z. P.; Lobanova, G. M.; Mikhailov, Y. N.; Schelokov, R. N. *Zh. Neorg. Khim.* **1990,** *35,* 3139. (b) Meyer, U.; Werner, H. *Chem. Ber.* **1990,** *123,* 697. (c) Langenbahn, M.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1990,** *397,* 347. (d) Aime, S.; Gervasio, G.; Milone, L.; Rosseti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1976,** 370.

(9) Bolshakov, A. M.; Ershova, M. M.; Glushkova, M. A.; Buslaev, Yu. A. *Koord. Khim.* **1978,** *4,* 1767.

(10) (a) Charalambous, J.; Haines, L. I. B.; Morgan, J. S.; Peat, D. S.; Campbell, M. J. M.; Bailey, J. *Polyhedron* **1987,** *6,* 1027. (b) Langenbahn, M.; Stoeckli-Evans, H.; Süss-Fink, G. *Helv. Chim. Acta* **1991,** *74,* 549.

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formation of metal-bounded organonitriles,[11a,b] or azavinylidene-type complexes.[11c] In high oxidation state metal ion complexes hydrolysis followed by oxidation is observed.[12]

In this work, the *cis*- and *trans*-$[Pt(Me_2C{=}NOH)_2Cl_n]$ (n = 2, 4) complexes were synthesized and their interconversions in the solid phase and in solution were studied. The coordinated oximes in *cis*-$[Pt(Me_2C{=}NOH)_2Cl_4]$ have been found not to be subjected to hydrolysis but to undergo an unusual Pt(IV)-mediated redox coupling.

Experimental Section

The complex $K_2[PtCl_4]$ and 2-propanone oxime were purchased from Reakhim. Elemental analysis was performed at the Analytical Chemistry Laboratories at the St. Petersburg State University. Melting (or decomposition) points were determined on a Kofler micro-hot-stage apparatus and were uncorrected. TGA measurements were carried out by means of the Paulik, Paulik, Erdey Model OD-102 derivatograph; samples were heated at 2 deg/min. IR spectra were recorded for KBr pellets using a Perkin-Elmer Model 983G spectrometer. ^1H, ^{13}C, and ^{195}Pt NMR spectra were recorded at 200.13, 50.324, and 64.386 MHz, respectively, on Bruker Models AC-200 (^1H, ^{13}C) and MSL-300 (^{195}Pt) spectrometers with a DMF-d_7 internal lock using 10-mm sample tubes, at an ambient temperature of 297 K. TMS and 1 M solutions of $Na_2[PtCl_6]$ in D_2O were used as external chemical shift references. Negative values denote low-frequency (high-field) shifts.

Syntheses of the Complexes. *cis*-$[Pt(Me_2C{=}NOH)_2Cl_2]$, 1. The preparation of this compound is based on a modification of a published method.[7] A solution of $K_2[PtCl_4]$ (1.98 g, 4.77 mmol) in water (20 mL) was placed into an Erlenmeyer flask, and 2-propanone oxime (0.69 g, 9.44 mmol) was added. The flask was stoppered, and the reaction mixture was stirred at 60–70 °C for 20 min, giving an orange-yellow solution which was then cooled to room temperature over 30 min. Pale-yellow crystals of *cis*-$[Pt(Me_2C{=}NOH)_2Cl_2]$ after cooling precipitated and were filtered off, washed with 2-propanol (2 mL) and ether (2 × 3 mL), and dried in air at 70 °C. Yield of **1**: 1.79 g, 91%, based on Pt.

Mp: 185–190 °C dec (lit.[7] mp 170–175 °C). Principal features of DTA/TG: 180–185 °C sharp exopeak (mass loss ca. 6%, sharp step); 220 °C exopeak (mass loss ca. 9%, extended step). Anal. Calcd for $C_6H_{14}Cl_2N_2O_2Pt$: Cl, 17.2; Pt, 47.3. Found: Cl, 17.2; Pt, 47.2. IR (selected bands, cm^{-1}): 3345 s, br, and/or 3246 s, br ν(OH), 1368 s δ(OH), 1658 m ν(C=N), 347 ms and 325 ms ν(Pt–Cl). ^1H NMR: 2.19 ($^4J_{PtH}$ = 8.0 Hz) and 2.65 ($^4J_{PtH}$ = 10.0 Hz) (CH_3), 9.95 ppm (OH). $^{13}C\{^1H\}$ NMR: 18.55 ($^3J_{PtC}$ = 22 Hz) and 24.68 ($^3J_{PtC}$ = 25.0 Hz) (CH_3), 166.94 ppm ($^2J_{PtC}$ = 52 Hz) (C=N). $^{195}Pt\{^1H\}$ NMR: −2100 ppm. Crystallographic parameters are monoclinic, space group $B2/b$, a = 11.074 (3), b = 16.114 (4), c = 8.177 (1) Å, γ = 111.76 (1)°, V = 1355.0 (5) Å^3, Z = 4.

***trans*-$[Pt(Me_2C{=}NOH)_2Cl_2]$, 2. (i)** Synthesis is based on a modification of a published method.[7] A solution of $K_2[PtCl_4]$ (2.05 g, 4.94 mmol) in water (20 mL) was placed into an open beaker, and 2-propanone oxime (3.50 g, 47.88 mmol) was added. The mixture was heated (90–95 °C) and water permitted to evaporate to half of the solution volume. On cooling to room temperature with continued stirring, pale yellow crystals of *trans*-$[Pt(Me_2C{=}NOH)_2Cl_2]$ precipitated. The solid was filtered off, washed on a filter with 2-propanol (2 mL) and ether (2 × 2 mL), and recrystallized from acetonitrile. Yield of **2**: 1.79 g, 88%, based on Pt.

(ii) By Cis–Trans Isomerization. Complex **1** completely isomerizes to **2** within 24 h in solutions of acetone or acetonitrile at 20–25 °C in the presence of a 0.1 M amount of 2-propanone oxime. Cis–trans isomerization can also occur on heating of the cis complex **1** in the solid phase (140 °C, 5 h) followed by the recrystallization of the product from acetonitrile.

Mp: 230–240 °C dec. Principal features of DTA/TG: 225 °C, sharp exopeak (mass loss ca. 15%, sharp step). Anal. Calcd for $C_6H_{14}Cl_2N_2O_2Pt$: Cl, 17.2; Pt, 47.3. Found: Cl, 17.2; Pt, 47.4. IR (selected bands, cm^{-1}): 3248 vs, br ν(OH), 1360 s δ(OH), 1662 m ν(C=N), 332 s ν(Pt—Cl). ^1H NMR: 2.17 ($^4J_{PtH}$ = 12.0 Hz) and 2.63 ($^4J_{PtH}$ = 10.0 Hz) (CH_3), 10.01 ppm (OH). $^{13}C\{^1H\}$ NMR: 18.17 and 24.20 (CH_3), 164.55 ppm (C=N). $^{195}Pt\{^1H\}$ NMR: −2104 ppm.

***cis*-$[Pt(Me_2C{=}NOH)(DMSO)Cl_2]$, 3. (i) Substitution of 2-Propanone Oxime in 1.** A solution of the complex **1** (1.82 g, 4.42 mmol) in acetone (30 mL) was placed into a round-bottomed flask equipped with a reflux condenser, and dimethyl sulfoxide (0.52 mL, 6.65 mmol) was added. The reaction mixture was boiled for 20 min, the solvent was removed in vacuo, and the precipitate was crystallized over ether. The obtained crystalline precipitate of **3** was filtered off, washed with ether (4 × 5 mL), and dried in air at 70 °C. Yield of **3**: 1.33 g, 72%, based on Pt.

(ii) By Trans–Cis Isomerization. Finely powdered complex **4** was spread as a uniform thin layer on a Petri dish, placed into an air thermostat, and heated at a rate 2 deg/min up to 160 °C. The complex was kept at 160 °C for 1 h to completion of the trans–cis conversion. To prepare a pure sample, the crude product should be recrystallized from nitromethane or acetonitrile. The trans–cis isomerization of **4** may also be performed in boiling acetonitrile for 30 min.

The complex was isolated from $MeNO_2$ as colorless (rapid crystallization) or pale-yellow (slow crystallization) rodlike crystals. Mp: 177–178 °C. DTA/TG characteristics are approximately as described.[6g] Anal. Calcd for $C_5H_{13}Cl_2NO_2PtS$: Cl, 17.0; Pt, 46.8. Found: Cl, 16.9; Pt, 46.9. IR (selected bands, cm^{-1}): 3207 s, br ν(OH), 1375 s δ(OH), 1664 m ν(C=N), 1117 s ν(S=O), 373 ms γ(CSO), 347 ms and 321 ms ν(Pt—Cl). ^1H NMR: 2.15 ($^4J_{PtH}$ = 8.0 Hz) and 2.56 ($^4J_{PtH}$ = 13.0 Hz) (CCH_3), 3.45 ($^3J_{PtH}$ = 23.0 Hz) and 3.47 ppm ($^3J_{PtH}$ = 23.0 Hz) (SCH_3). $^{13}C\{^1H\}$ NMR: 18.54 and 25.12 ($C\mathit{C}H_3$), 44.55 ($^2J_{PtC}$ = 60 Hz) and 40.98 (SCH_3), 164.84 ppm (C=N). $^{195}Pt\{^1H\}$ NMR: −2899 ppm.

***trans*-$[Pt(Me_2C{=}NOH)(DMSO)Cl_2]$, 4.** To a solution of $K_2[PtCl_4]$ (0.38 g, 0.92 mmol) in water (20 mL) was added dimethyl sulfoxide (0.075 mL, 0.96 mmol). The solution was heated, about half of the solvent removed by boiling, the solution cooled to room temperature, and 2-propanone oxime (0.07 g, 0.96 mmol) added. The reaction mixture was stirred vigorously for 10 min, and then the precipitate was filtered off, washed with 2-propanol (3 × 5 mL) and ether (3 × 5 mL), and dried in air at 70 °C. Yield of **4**: 0.30 g, 78%, based on Pt.

The complex was obtained as yellow crystals. This compound melts at 148–152 °C and crystallizes from the melt; subsequent remelting is observed at 177–180 °C. DTA/TG characteristics are approximately as described.[6g] Anal. Calcd for $C_5H_{13}Cl_2NO_2PtS$: Cl, 17.0; Pt, 46.8. Found: Cl, 17.1; Pt, 46.3. IR (selected bands, cm^{-1}): 3374 s, br ν(OH), 1365 s δ(OH), 1669 m ν(C=N), 1130 vs ν(S=O), 384 ms γ(CSO), 339 ms ν(Pt—Cl). ^1H NMR: 2.18 ($^4J_{PtH}$ = 8.0 Hz) and 2.50 ($^4J_{PtH}$ = 11.0 Hz) (CCH_3), 3.34 ($^3J_{PtH}$ = 22.0 Hz) (SCH_3), 10.59 ppm ($^3J_{PtH}$ = 48.0 Hz) (OH). $^{13}C\{^1H\}$ NMR: 18.31 ($^3J_{PtC}$ = 14 Hz) and 24.18 ($^3J_{PtC}$ = 22 Hz) ($C\mathit{C}H_3$), 43.13 ($^2J_{PtC}$ = 58 Hz) (SCH_3), 164.91 ppm ($^2J_{PtC}$ = 44 Hz) (C=N). $^{195}Pt\{^1H\}$ NMR: −3042 ppm.

***cis*-$[Pt(Me_2C{=}NOH)_2Cl_4]$, 5, and *trans*-$[Pt(Me_2C{=}NOH)_2Cl_4]$, 6.** Cl_2 was bubbled respectively for 5 and 15 min via suspension of complexes **1** or **2** in chloroform (ca. 2 g of the complex in 8–10 mL). The mixture homogenized with the formation of bright-yellow solutions. The solvent was rapidly removed in vacuo, and the residue was crystallized over 2-propanol, filtered, washed with 2-propanol (3 × 5 mL) and ether (3 × 5 mL), and dried in air at 70 °C. Yield: 75–85%.

Complex **5** was isolated as bright-yellow crystals. Mp: 148–153 °C. Principal features of DTA/TG: 90–95 °C small broad endopeak (mass loss ca. 5%, extended step); 145–150 °C exopeak (mass loss ca. 15%). Anal. Calcd for $C_6H_{14}Cl_4N_2O_2Pt$: Cl, 29.4; Pt, 40.4. Found: Cl, 28.8; Pt, 40.3. IR (selected bands, cm^{-1}): 3347 s, br ν(OH), 1386 s δ(OH), 1635 m ν(C=N), 351 s ν(Pt—Cl). ^1H NMR: 2.47 ($^4J_{PtH}$ = 6.5 Hz) and 2.63 ($^4J_{PtH}$ = 7.5 Hz) (CH_3), 9.55 ppm (OH). $^{13}C\{^1H\}$ NMR: 23.02 ($^3J_{PtC}$ = 14 Hz) and 25.21 ($^3J_{PtC}$ = 10 Hz) (CH_3), 177.84 ppm ($^2J_{PtC}$ = 30 Hz) (C=N). $^{195}Pt\{^1H\}$ NMR: 207 ppm. TLC on SiO_2 (Czecho-Slovakian Silufol UV 254 plates) in $CHCl_3$: R_f(*cis*-**5**) = 0.16, R_f(*trans*-**6**) = 0.74.

Complex **6** was isolated as bright-yellow crystals. Mp: 187–190 °C. Principal features of DTA/TG: 170 °C sharp exopeak (mass loss ca. 23%, very sharp step); 230 °C broad exopeak (mass loss ca. 18%, extended step). Anal. Calcd for $C_6H_{14}Cl_4N_2O_2Pt$: Cl, 29.4; Pt, 40.4. Found: Cl, 28.9; Pt, 39.8. IR (selected bands, cm^{-1}): 3349 s, br ν(OH), 1375 vs δ(OH), 1633 m ν(C=N), 344 s ν(Pt—Cl). ^1H NMR: 2.50 ($^4J_{PtH}$ = 7.0 Hz) and 2.77 ($^4J_{PtH}$ = 8.0 Hz) (CH_3), 9.17 ppm (OH). $^{13}C\{^1H\}$ NMR: 23.50 ($^3J_{PtC}$ = 16 Hz) and 26.47 ($^3J_{PtC}$ = 10 Hz) (CH_3), 178.16 ppm (C=N). $^{195}Pt\{^1H\}$ NMR: 129 ppm.

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(11) (a) Kaneda, K.; Doken, K.; Imanaka, T. *Chem. Lett.* **1988**, 285. (b) Olczak-Kobza, M. *Thermochim. Acta* **1988**, *A133*, 347. (c) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem.* **1987**, *99*, 277.

(12) (a) Bleaupre, P. W.; Holland, W. J. *Mikrochim. Acta* **1983**, *3*, 341. (b) Tananaev, I. G.; Shilov, V. P.; Krot, N. N. *Radiokhimia* **1986**, *28*, 92. (c) Shilov, V. P.; Krot, N. N.; Stepanova, E. S. *Radiokhimia* **1976**, *18*, 355.

(13) A preliminary communication concerning part of the work has appeared: Kukushkin, V. Yu.; Belsky, V. K.; Konovalov, V. E.; Aleksandrova, E. A.; Pankova, E. Yu. *Zh. Obsch. Khim.* **1991**, *61*, 254.

Table I. Crystal Data for 7

chemical formula	$C_6H_{12}Cl_2N_2O_2Pt$
a, Å	8.860 (3)
b, Å	8.022 (2)
c, Å	15.744 (4)
V, Å^3	1119.0 (6)
Z	4
formula weight	410.17
space group	$Pn2_1a$ (No. 33)
T, °C	25
λ, Å	0.710 69
ρ_{calcd}, g cm^{-3}	2.43
μ, cm^{-1}	136.25
range of transmission factor	0.152–0.364
R(merge)	0.0359
R^a	0.043
$R_w{}^b$	0.042

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

[Pt(N(=O)CMe₂ONCMe₂)Cl₂], 7. Water (20 mL) was added dropwise for 2–3 min to the bright-yellow solution of *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] (0.85 g) in acetone (20 mL). After addition of the first drops, the solution became dark-red and precipitation took place at the end of the addition of water. The reaction mixture was kept in the open beaker for 3 h, and then the precipitate was filtered off, washed on the filter with 2-propanol (3 × 5 mL) and ether (3 × 5 mL), and dried in air at 20–25 °C. Yield of 7: 0.52 g, 72%, based on Pt.

The complex was isolated as dark-red needlelike crystals. On heating at the solid phase, this compound decomposes without melting at 190–210 °C. Principal features of DTA/TG: 120–125 °C exopeak (mass loss ca. 35%, sharp step); 190 °C exopeak (extended step of mass loss). Anal. Calcd for $C_6H_{12}Cl_2N_2O_2Pt$: Cl, 17.3; Pt, 47.6. Found: Cl, 17.1; Pt, 47.9. IR (selected bands, cm^{-1}): 1625 m ν(C=N), 1542 vs ν(N=O), 354 sm and 335 sm ν(Pt—Cl). ^{1}H NMR: 1.54 (OC(CH$_3$)), 2.62 ($^4J_{PtH}$ = 8.5 Hz) and 2.70 ppm ($^4J_{PtH}$ = 10.0 Hz) (N=C(CH$_3$)$_2$). ^{13}C{^{1}H} NMR: 20.88 (OC(*C*H$_3$)$_2$), 22.98 and 24.81 (N=C(*C*H$_3$)$_2$), 126.04 (O*C*(CH$_3$)$_2$), 183.12 ppm (N=*C*(CH$_3$)$_2$). ^{195}Pt{^{1}H} NMR: −2104 ppm.

X-ray Structure Determination of the [Pt(N(=O)CMe₂ONCMe₂)Cl₂] Complex. Diffraction data were collected on a Syntex $P\bar{1}$ diffractometer, using MoKα radiation (λ = 0.710 69 Å), β-filter; cell parameters were obtained from 14 centered reflections with 2θ between 24° and 28°, 1788 independent reflections were of which 927 with $I \geq 3\sigma(I)$ measured up to 50° by the $\theta/2\theta$ scan technique. The scan speed was 3.4–12.0° min^{-1}; the ranges of *hkl* were h = 0–10, k = 0–10, and l = 0–17. Standard reflections 200, 040, 006 were measured every 100 reflections and showed no change with time. Diffractometer data were processed by the program PROFIT[14] with profile analysis of reflections. The structure was solved by means of Fourier synthesis based upon the Pt atom coordinates obtained from the Patterson synthesis and refined by full-matrix least squares based on F with weights $w = 1/\sigma^2(F) + 0.002F^2$. All non-hydrogen atoms were treated anisotropically. H atoms were not treated. The extinction correction was not made. R = 0.043, R_w = 0.042, and S = 1.004. Lorentz polarization and absorption corrections were made. The crystal size was 0.27 × 0.08 × 0.08 mm; the crystal faces were (100), (011), (01̄1). Calculation was carried out with SHELXTL[15] on a Nova-3 computer. Scattering factors are from *International Tables for X-ray Crystallography*.[16] Crystal data and atomic parameters are given in Tables I and II; bond distances and angles are given in Tables III and IV.

Discussion

Synthesis and Isomerization of the *cis*- and *trans*-[Pt(Me₂C=NOH)₂Cl₂] Complexes. On the basis of the data in ref 7, the *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] complex was prepared by the reaction of K$_2$[PtCl$_4$] with 2-propanone oxime in ~1:2 reagent molar ratio in water solution. The solid-phase isomerization of Pt(II) complexes occurs fairly often on the DTA curves as paired endo and exo peaks not related to the mass loss of a sample. On the thermogram of *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] such effects are absent. The isomerization was observed as a result of the stepwise temperature increase in the heating with TLC and IR monitoring of the substance following each heating step. Heating of *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] in an air thermostat at 140 °C for 5 h was found to lead to the solid-phase cis → trans isomerization.[17] This reaction can be used as a simple method of preparation of *trans*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$]. The latter had been prepared earlier as a result of the replacement of acetoximes in [Pt(Me$_2$C=NOH)$_4$]Cl$_2$ or in [Pt(Me$_2$C=NOH)$_3$Cl]Cl on fairly long heating of the compound in concentrated HCl.[18]

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for 7

atom	x	y	z	U
Pt	1997 (1)	1924 (19)	7388 (1)	46 (1)
Cl(1)	2091 (4)	458 (21)	6159 (3)	65 (2)
Cl(2)	1546 (8)	4342 (20)	6606 (4)	88 (2)
O(1)	1273 (25)	4538 (35)	8585 (12)	106 (7)
O(2)	1599 (13)	310 (25)	8949 (7)	54 (4)
N(1)	1707 (18)	3106 (34)	8419 (13)	71 (6)
N(2)	2443 (17)	96 (27)	8181 (8)	46 (4)
C(1)	1821 (15)	2144 (35)	9238 (10)	49 (5)
C(2)	538 (19)	2340 (32)	9868 (11)	89 (8)
C(3)	3405 (18)	2279 (35)	9577 (10)	68 (7)
C(4)	3329 (23)	−2229 (29)	9020 (12)	73 (7)
C(5)	3204 (16)	−1194 (27)	8245 (10)	47 (5)
C(6)	4122 (25)	−1842 (33)	7473 (9)	58 (5)

Table III. Bond Lengths (Å) for 7

Pt–Cl(1)	2.27 (1)	Pr–Cl(2)	2.33 (2)
Pt–N(1)	1.90 (2)	Pt–N(2)	1.97 (2)
O(1)–N(1)	1.24 (4)	O(2)–N(2)	1.43 (2)
O(2)–C(1)	1.55 (3)	N(1)–C(1)	1.51 (3)
N(2)–C(5)	1.24 (3)	C(1)–C(2)	1.52 (2)
C(1)–C(3)	1.51 (2)	C(4)–C(5)	1.48 (3)
C(5)–C(6)	1.55 (2)		

Table IV. Bond Angles (deg) for 7

Cl(1)–Pt–Cl(2)	89.2 (5)	Cl(1)–Pt–N(1)	174.2 (5)
Cl(2)–Pt–N(1)	91 (1)	Cl(1)–Pt–N(1)	98.5 (9)
Cl(2)–Pt–N(2)	172.0 (8)	N(1)–Pt–N(2)	81.8 (9)
N(2)–O(2)–C(1)	107 (1)	Pt–N(1)–O(1)	133 (2)
Pt–N(1)–C(1)	118 (2)	O(1)–N(1)–C(1)	108 (2)
Pt–N(2)–O(2)	110 (1)	Pt–N(2)–C(5)	142 (1)
O(2)–N(2)–C(5)	108 (2)	O(2)–C(1)–N(1)	103 (2)
O(2)–C(1)–C(2)	101 (2)	N(1)–C(1)–C(2)	117 (2)
O(2)–C(1)–C(3)	107 (2)	N(1)–C(1)–C(3)	109 (2)
C(2)–C(1)–C(3)	117 (1)	N(2)–C(5)–C(4)	125 (2)
N(2)–C(5)–C(6)	120 (2)	C(4)–C(5)–C(6)	115 (2)

The geometrical isomerization of [Pt(Me$_2$C=NOH)$_2$Cl$_2$] proceeded without significant decomposition as also in acetonitrile or acetone solutions at 20–25 °C containing catalytic amounts of Me$_2$C=NOH. On boiling these solutions, the cis → trans conversion of [Pt(Me$_2$C=NOH)$_2$Cl$_2$] is accompanied by a side reaction, producing a nonidentified product. Heating of *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] in DMF solution containing a 1:1 stoichiometric amount of DMSO leads to the replacement of 2-propanone oxime by dimethyl sulfoxide with the formation of *cis*- and *trans*-[Pt(Me$_2$C=NOH)(DMSO)Cl$_2$]. The latter was independently prepared from K[Pt(DMSO)Cl$_3$] and Me$_2$C=NOH; *cis*-[Pt(Me$_2$C=NOH)(DMSO)Cl$_2$] resulted from the solid-phase thermal isomerization of the trans isomer.[6g]

The substitution reaction of 2-propanone oxime by dimethyl sulfoxide molecules in *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] proceeds efficiently in DMF even at a 1:1 "complex:DMSO" molar ratio. On solution of *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] in DMSO at room temperature both oxime ligands are replaced, forming the well-

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(14) Strel'tsov, V. A.; Zavodnik, V. E. *Kristallografia* **1989**, *34*, 1369.

(15) Sheldrick, G. M. *SHELXTL Program Library*, Revision 4.1; Nicolet Instrument Corp.: Madison, WI, 1983.

(16) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

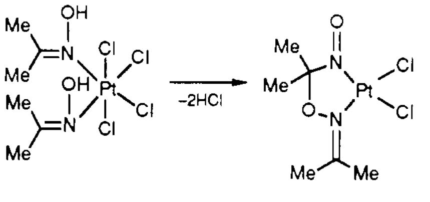
(17) Kukushkin, V. Yu.; Kukushkin, Yu. N. *Theory and Practice of Coordination Compounds Synthesis*; Nauka: Leningrad, 1990; p 246.

(18) *Synthesis of Complex Compounds of Platinum Group Metals* (*Sintez Kompleksnih Soedinenii Metallov Platinovoy Gruppy*); Chernyaev, I. I., Ed.; Nauka Publishers: Moscow, 1964; pp 58–60.

known *cis*-[Pt(DMSO)$_2$Cl$_2$].[19,20]

The isomerization of complexes of the type [Pt(amine)$_2$X$_2$] have been studied by many scientific groups both in the solid phase and in solution. In part the interest in these processes is due to the anticancer activity of *cis*-[Pt(NH$_3$)$_2$Cl$_2$] and other compounds of the type [PtL$_2$X$_2$] (L = N-donor ligand[21]). Despite a fairly large number of studies concerning the cis–trans isomerization of complexes [PtL$_2$X$_2$] (L = NH$_3$[22] and other sp^3-type ligands;[23] L = heterocyclic sp^2-type N-donor ligands[24] and organonitriles;[25,26] X = acidoligands), to our knowledge, only a single paper deals with cis–trans isomerization of the oxime complex [Pt(C$_5$H$_8$NOH)$_2$Cl$_2$].[27]

Synthesis of *cis*- and *trans*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] and Redox Coupling of Oximes in *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$]. The oxidative addition of Cl$_2$ to the *cis*- or *trans*-[Pt(Me$_2$C=NOH)$_2$Cl$_2$] complexes leads to formation of *cis*- or *trans*-[Pt(Me$_2$C=NOH)$_2$-Cl$_4$]. The latter were isolated as bright-yellow crystals and were characterized by elemental analysis and IR and NMR spectroscopy (see Experimental Section). The trans complex is fairly stable in an acetone–water mixture, and no significant transformations are observed at room temperature over a 3-h period. The cis compound exhibits a different behavior. *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] undergoes a complete transformation in 3 h in aqueous acetone: the color of the solution changes from yellow to dark red. Further addition of water to the mixture results in formation of a solid. On the basis of the elemental analysis, IR spectra, and NMR spectra (see Experimental Section) and the X-ray structure analysis (Figure 1), this is identified as [Pt(N(=O)CMe$_2$ONCMe$_2$)Cl$_2$]. Thus, the *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] in solution is subject to a Pt(IV)-mediated redox coupling of 2-propanone oximes. The overall reaction is described by the following scheme:



The coordination of 2-propanone oxime (p$K_a \approx 12$) even to the Pt(II) ion increases acidity by more than 6 orders.[6a] By analogy with the published data[5,28] it suggests that acidity of 2-propanone oxime in the Pt(IV) complexes will be higher than that in similar Pt(II) complexes. We believe the formation of [Pt(N(=O)-CMe$_2$ONCMe$_2$)Cl$_2$] includes a deprotonation of a coordinated 2-propanone oxime, leading to the increase of its nucleophility;[29] anionic oxygen then attacks a carbon atom of an adjacent ligand; ring closure is followed by an overall $2e^-$ oxidation of the formed chelate and an overall $2e^-$ reduction to Pt(II). Apparently, the redox coupling of ligands in *trans*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] does not take place because the oximes are too far removed from each other.

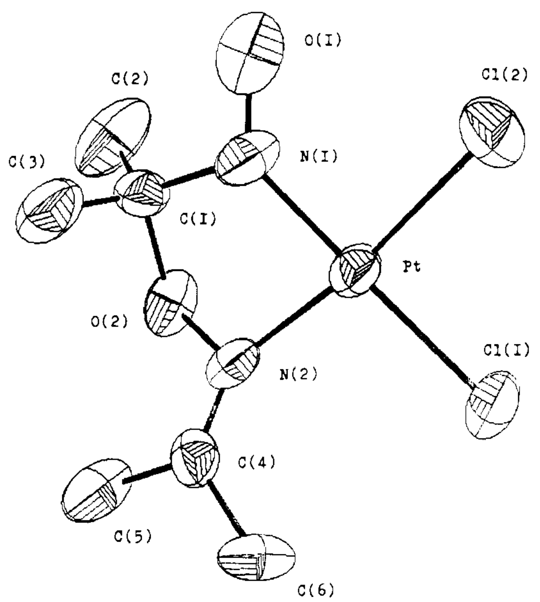


Figure 1. Perspective view of 7. Thermal ellipsoids are drawn at the 50% probability level.

Description of the Structure of [Pt(N(=O)CMe$_2$ONCMe$_2$)-Cl$_2$] (7). In complex 7 the coordination polyhedron of the Pt atom is a slightly distorted square plane. The displacement of the Pt, Cl(1), Cl(2), N(1), and N(2) atoms from the least-squares plane passing through these atoms equals 0.023, −0.068, 0.062, −0.092, and 0.074 Å, respectively. The sign and value of these atomic displacements from the coordination plane suggest slight tetrahedral distortion.

Complex 7 provides the third example[30,31] of a compound with the nitrosoalkyl ligand for which the X-ray structure was determined. The Pt—N(1) bond length is 1.90 (2) Å. This interatomic distance is consistent with that of Pt=N in the [Pt(N(O)Bu)Cl(CH$_2$CHN(O)Bu)] (1.90 (2) Å[30]); in the *trans*-[Pt(N(O)Bu)$_2$Cl$_2$] the Pt—N bond is 1.967 (9) Å.[31] In 7 the N(1)—O(1) bond length equals 1.24 (4) Å which within the 3σ coincides with that of N=O in [Pt(N(O)Bu)Cl(CH$_2$CH$_2$-N(O)Bu)] (1.22 (2) Å[30]) and *trans*-[Pt(N(O)Bu)$_2$Cl$_2$] (1.21 (1) Å[31]).

In the chelate ligand, the N=CMe$_2$ fragment is planar. It is twisted 27.5° relative to the coordinated plane. The Pt—N(2) interatomic distance in 7 is 1.97 (2) Å which is consistent with those in the complex [Pt(*N*,*N*—N(=CMe$_2$)C$_2$H$_4$NH$_2$)(PBu$_3$)-Cl]Cl (2.08 (1) Å[32]) and in some oxime-containing Pt(II)

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(19) Shibaeva, R. P. *Koord. Khim.* **1985**, *11*, 129.

(20) (a) Annibale, G.; Bonivento, M.; Canovese, L.; Cattalini, L.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1985**, *24*, 797. (b) Melanson, R.; Rochon, F. D. *Can. J. Chem.* **1975**, *53*, 2371.

(21) For reviews, see: (a) Farrell, N. Transition Metal Complexes as Drugs and Chemotherapeutic Agents. In *Catalysis by Metal Complexes*; James, B. R., Ugo, R., Eds.; Reidel-Kluwer: Dordrecht, The Netherlands, 1989; Vol. 11, pp 304. (b) *Platinum, gold and other metal chemotherapeutic agents*; Lippard, S. J., Ed.; ACS Symposium Series 209; American Chemical Society: Washington, DC, 1983. (c) Reedijk, J. *Pure Appl. Chem.* **1987**, *59*, 181. (d) Reedijk, J.; Fichtinger-Schepman, A. H. J.; Van Oosteron, A. T.; Van de Putte, P. *Struct. Bonding (Berlin)* **1987**, *67*, 53.

(22) Roe, S. P.; Hill, J. O.; Magel, R. J. *Inorg. Chim. Acta* **1986**, *115*, L15 and references therein.

(23) (a) Faraglia, G.; Sindellari, L.; Sitran, S. *Thermochim. Acta* **1987**, *115*, 229. (b) Faraglia, G.; Sindellari, L.; Cherch, V. *Transition Met. Chem.* **1986**, *11*, 98. (c) Kong, P.-C.; Rochon, F. D. *Inorg. Chim. Acta* **1984**, *83*, 65. (d) Kukushkin, Yu. N.; Fedotova, G. P.; Ustratova, V. F.; Postnikova, E. S. *Zh. Neorg. Khim.* **1979**, *24*, 730.

(24) (a) Kuduk-Jaworska, J. *Polish J. Chem.* **1985**, *59*, 705. (b) Kong, P.-C.; Rochon, F. D. *Can. J. Chem.* **1979**, *57*, 526. (c) Kukushkin, Yu. N.; Abdurakhmanov, R. O.; Kiseleva, N. P. *Zh. Neorg. Khim.* **1986**, *31*, 2175.

(25) (a) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 199. (b) Kukushkin, V. Yu.; Tkachuk, V. M.; Vorobiov-Desiatovsky, N. V. *Inorg. Synth.*, in press.

(26) Kukushkin, V. Yu.; Tkachuk, V. M. *Z. Anorg. Allg. Chem.*, in press

(27) Kukushkin, Yu. N.; Strelin, S. G.; Byankina, L. S.; Bakhireva, S. I. *Zh. Neorg. Khim.* **1977**, *22*, 1720.

(28) Evans, I. P.; Everett, G. W.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1975**, 139.

(29) Aubort, J. D.; Hudson, R. F.; Woodcock, R. C. *Tetrahedron Lett.* **1973**, 2229.

(30) Mansuy, D.; Dreme, M.; Chottard, J.-C.; Girault, J.-P.; Guilhem, J. *J. Am. Chem. Soc.* **1980**, *102*, 844.

(31) Mansuy, D.; Dreme, M.; Chottard, J. C.; Guilhem, J. *J. Organomet. Chem.* **1978**, *161*, 207.

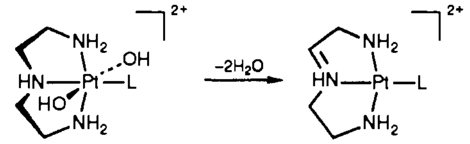
(32) Kozelka, J.; Bois, C. *Inorg. Chem.* **1988**, *27*, 3866.

complexes (1.97–2.02 Å[33]). The Pt—Cl bond lengths (2.27 (1) and 2.33 (2) Å) are not significantly different. Apparently, this may be attributed to a different trans or cis influence of nitrosoalkyl and alkyloxime parts of the ligand. However, the fairly large standard deviations and the absence of data on the structures of the complexes containing the L—Pt—Cl (L = N(O)R, N(OR′)CR$_2$) entity prevents a more decisive conclusion about the relative trans and/or cis influences of nitrosoalkyls and alkyloximes in the Pt(II) complexes.

The IR and NMR data of 7 are in agreement with the X-ray structure (see Experimental Section). It is noteworthy that 7 is red in color which is unusual for [Pt^{II}L$_2$X$_2$] complexes. The other published platinum(II) nitrosoalkyl complexes[30,31] are also observed to be red.

Concluding Remarks

Other examples of an oxidation of ligands with concomitant reduction of metal ion in the Pt(IV) complexes may be cited. For instance, the deprotonation of coordinated hydroxylamine in the [Pt(NH$_2$OH)$_2$X$_4$] (X = Cl, Br) complexes is known to result in the formation of N$_2$O and the Pt(II) compounds.[34] We also cite the autoredox of acido ligands in K$_2$[PtX$_6$] (X = SCN,[35] J[36]) leading to K$_2$[PtX$_4$] accompanied by abstraction of X$_2$. Thermolysis of pyridine complex [Pt^{IV}Py$_2$Cl$_4$] gives [Pt^{II}(2,2′-bipyridyl)Cl$_2$] as byproduct.[37] Finally, B. Lippert et al.[38] have published an example of an unusual dehydrogenation of a diethylenetriamine ligand in a Pt(IV) complex followed by reductive elimination at the metal center and a simultaneous oxidation of the ligand:



L = 1-methylcytosine

In conclusion it should be mentioned that the process of redox coupling of oximes in *cis*-[Pt(Me$_2$C=NOH)$_2$Cl$_4$] has analogs in the chemistry of other transition metals. Fairly recently a process of oxidative coupling of iminoacyl groups in an Mn(I) complex leading to a diazabutadiene derivative of Mn(0) has been reported.[39]

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Supplementary Material Available: Figure showing a view of the unit cell of 7 and tables of anisotropic temperature factors, hydrogen coordinates, and temperature factors (2 pages). Ordering information is given on any current masthead page.

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(33) (a) Megnamisi-Belombe, M. *J. Solid State Chem.* **1979**, *27*, 389. (b) Endres, H.; Megnamisi-Belombe, M.; Keller, H. J.; Weiss, J. *Acta Crystallogr., Sect. B* **1976**, *32*, 457. (c) Ferraris, G.; Viterbo, D. *Acta Crystallogr., Sect. B* **1969**, *25*, 2066. (d) Schelemper, E. O. *Inorg. Chem.* **1969**, *8*, 2740. (e) Pritzkow, H. *Z. Naturforsch.* **1976**, *31b*, 401. (f) Kaitano, Y.; Kobori, K.; Tanimura, M.; Kinoshita, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2969.

(34) Stetsenko, A. I.; Abzaeva, T. G.; Yakovlev, K. I.; Mitkinova, N. D. *Koord. Khim.* **1977**, *3*, 1722.

(35) Jezowska-Trzebiatowska, B.; Ostern, M.; Wronska, M.; Biernat, J. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1966**, *14*, 807.

(36) Grinberg, A. A.; Ptitsin, B. V.; Lavrentev, V. N. *Zh. Phys. Khim.* **1937**, *10*, 661.

(37) (a) Sokolenko, V. A.; Bondarenko, V. S.; Korniets, E. D.; Kovrova, N. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 1692. (b) Sokolenko, V. A.; Bondarenko, V. S.; Korniets, E. D.; Kovtonuk, N. P.; Kovrova, N. B. *Zh. Neorg. Khim.* **1989**, *34*, 1537. (c) Bondarenko, V. S.; Korniets, E. D.; Sokolenko, V. A.; Kovrova, N. B.; Kovtonuk, N. P. *Zh. Neorg. Khim.* **1989**, *34*, 1541.

(38) Schwarz, F.; Schöllhorn, H.; Thewalt, U.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1282.

(39) Motz, P. L.; Williams, J. P.; Alexander, J. J.; Ho, D. M.; Ricci, J. S.; Miller, W. T. *Organometallics* **1989**, *8*, 1523.