An efficient method for selective oxidation of (oxime)Pt(II) to (oxime)Pt(IV) species using *N*,*N*-dichlorotosylamide

Anastasiia M. Afanasenko[1] • Evgeny Yu. Bulatov[2] • Tatiana G. Chulkova[1] • Matti Haukka[2] • Fedor M. Dolgushin[3]

✉ Tatiana G. Chulkova

t.chulkova@spbu.ru

[1] Institute of Chemistry, Saint Petersburg State University, Universitetskiy Pr., 26, 198504 Stary Petergof, Russian Federation

[2] Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland

[3] A.N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Street, 119991 Moscow, Russian Federation

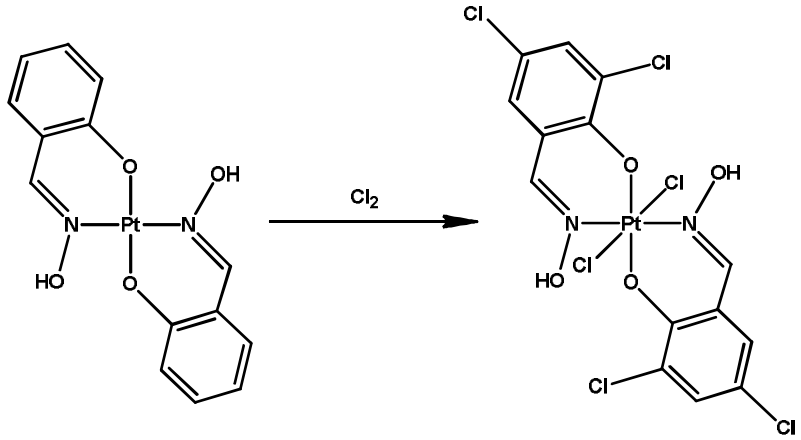
Abstract

The oxidation of (oxime)Pt^{II} species using the electrophilic chlorine based oxidant *N*,*N*-dichlorotosylamide (4-$CH_3C_6H_4SO_2NCl_2$) was studied. The reactions of *trans*-[$PtCl_2$(oxime)$_2$] (where oxime = acetoxime, cyclopentanone oxime, or acetaldoxime) with this oxidant lead to *trans*-[$PtCl_4$(oxime)$_2$] products. The oxidation of *trans*-[Pt(*o*-$OC_6H_4CH=NOH)_2$] at room temperature gave *trans*-[$PtCl_2$(*o*-$OC_6H_4CH=NOH)_2$], whereas the same reaction upon heating was accompanied by electrophilic substitution of the benzene rings.

Keywords: Chlorination, Ligand reactivity, Oximes, Platinum complexes

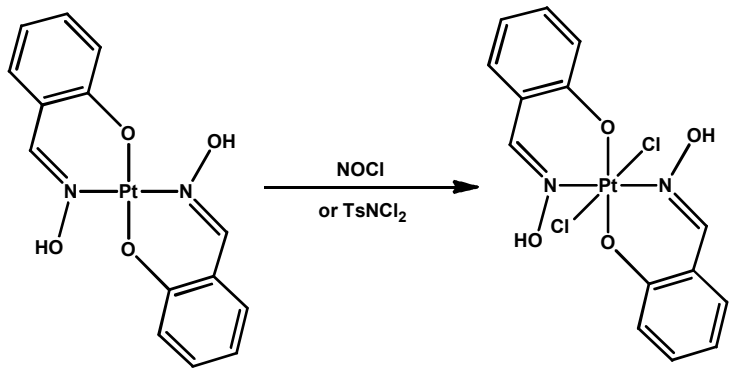
Introduction

The oxidations of Pt^{II} species with a variety of electrophilic chlorinating reagents have been reported. The oxidative chlorination of platinum(II) species by molecular chlorine is a common method of synthesis of platinum(IV) complexes [1]. The reactions with Cl_2 proceed via oxidative addition to the metal center with formation of the appropriate Pt^{IV} complexes. In particular, the platinum(II) complexes $[PtCl_2(RR'CNOH)_2]$ are converted into $[PtCl_4(RR'CNOH)_2]$ by treatment with Cl_2. The oxime ligands usually remain intact; however, in some cases, the ligands also react with molecular chlorine, and, e.g., passage of Cl_2 through a chloroform solution of $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$ resulted in both the oxidative addition of chlorine to the platinum(II) center and chlorination of the benzene ring (Scheme 1) [2].



Scheme 1 Chlorination of $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$ with Cl_2.

Overall, the platinum(IV) complex $[PtCl_2(2\text{-}O\text{-}3,5\text{-}Cl_2C_6H_2CH{=}NOH)_2]$ was isolated in 85% yield. In contrast to molecular chlorine, NOCl is a more selective chlorination agent. Oxidation of the metal center occurred selectively when nitrosyl chloride was used instead of Cl_2, giving $[PtCl_2(o\text{-}OC_6H_4CH{=}NOH)_2]$ without any chlorination of the benzene rings (Scheme 2) [2].



Scheme 2 Chlorination of [Pt(*o*-$OC_6H_4CH{=}NOH)_2$] with NOCl and $TsNCl_2$.

However, like chlorine, nitrosyl chloride is a highly toxic gas and this property restricts the usage of these reagents. While the reactions of (oxime)Pt^{II} species with other electrophilic chlorinating reagents have not been previously reported, related transformations of Pt^{II} to Pt^{IV} (or Pt^{III}) with various chlorinating oxidants have been documented. The oxidations of Pt^{II} complexes with iodobenzene dichloride ($PhICl_2$) [3-5], *N*-chlorosuccinimide (NCS) [5, 6], *N*,*N*-dichlorobenzenesulphonamide ($PhSO_2NCl_2$) [7], PCl_5 [8], and $SbCl_5$ [9] have been described.

In this study, we used *N*,*N*-dichlorotosylamide as a chlorinating agent for the selective chlorination of [$PtCl_2$(oxime)$_2$] complexes. *N*,*N*-Dichlorotosylamide is a relatively active solid reagent, which can be used as a stoichiometric solid chlorine equivalent providing selective oxidation of Pt(II) centers. This reagent is more convenient to use than chlorine and also more stable at room temperature than hypervalent iodine reagents.

Experimental

Materials and Instrumentation

All reagents and solvents were commercially available and used as received without further purification. *N*,*N*-Dichlorotosylamide (dichloramine T) was purchased from Sigma-Aldrich. FTIR spectra were recorded on Shimadzu FTIR-8400S (4000 – 400 cm^{-1}) and IRAffinity-1S (4000 – 300 cm^{-1}) spectrometers using KBr pellets. ^{1}H NMR measurements were performed on a Bruker-DPX 400 instrument at ambient temperature. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source using MeOH as the solvent. The instrument was operated in both positive and negative ion modes using a *m/z* range of 50 – 3000. The capillary voltage of the ion source was set at –4500 V (ESI^+– MS) or 3500 V (ESI^-– MS) and the capillary exit at ±(70 – 150) V. The nebulizer gas flow was 0.4 bar and drying gas flow 4.0 L/min. In the isotopic patterns, the most intense peak is reported.

Syntheses

Trans-[$PtCl_2$(acetoxime)$_2$] (**1**) [10, 11], *trans*-[$PtCl_2$(acetaldoxime)$_2$] (**2**) [12], *trans*-[$PtCl_2$(cyclopentanone oxime)$_2$] (**3**) [10], and *trans*-[Pt(*o*-$OC_6H_4CH{=}NOH)_2$] (**4**) [13] were obtained according to the published methods.

Synthesis of **5**–**7**. Full details are provided for *trans*-[$PtCl_4$(acetoxime)$_2$] (**5**); *trans*-[$PtCl_4$(acetaldoxime)$_2$] (**6**) and *trans*-[$PtCl_4$(cyclopentanone oxime)$_2$] (**7**) were synthesized by analogous procedures.

Complex **5**: Complex **1** (0.019 g, 0.045 mmol) and *N*,*N*-dichlorotosylamide (0.011 g, 0.045 mmol) were suspended in chloroform (5 mL). The reaction mixture was refluxed for 2 h, after which the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (60 Å; Merck) with chloroform as the eluent to give pure complex **5** as a yellow solid (R_f 0.59). Yield: 78%. M. P. = 189–191 °C (dec.). ^{1}H NMR ($CDCl_3$), δ (ppm): 9.08 (s, 2H, $^3J_{HPt}$ = 4.4 Hz, OH), 2.81 (s, 6H, $^4J_{HPt}$ = 8.0 Hz, CH_3), 2.50 (s, 6H, $^4J_{HPt}$ = 7.2 Hz, CH_3). IR (cm^{-1}): 3350 w *ν*(O–H), 1635 w *ν*(C=N). Anal. Calcd. for $C_6H_{14}Cl_4N_2O_2Pt$: C, 14.9; H, 2.9; N, 5.8. Found: C, 14.9; H, 2.9; N, 5.9%.

Complex **6**: Yield: 71%. R_f 0.61. Crystals suitable for X-ray diffraction were grown from a concentrated chloroform solution. Yellow crystals. M. p. = 174–176 °C (dec.). ^{1}H NMR ($CDCl_3$), δ (ppm): 9.37 (s, 2H, OH), 8.04 (q, 2H, $^3J_{HH}$ = 5.6 Hz, CH), 2.47 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH_3). IR (cm^{-1}): 3279 s *ν*(O–H), 1654 m *ν*(C=N). Anal. Calcd. for $C_4H_{10}Cl_4N_2O_2Pt$: C, 10.6; H, 2.2; N, 6.2. Found: C, 10.5; H, 2.6; N, 6.2%.

Complex **7**: Yield: 83%. R_f 0.56. Crystals suitable for X-ray diffraction were grown from a concentrated chloroform solution. Yellow crystals. M. p. = 196–199 °C (dec.). ^{1}H NMR ($CDCl_3$), δ (ppm): 9.06 (s, 2H, $^3J_{HPt}$ = 5.1 Hz, OH), 3.52 (t, 4H, $^3J_{HH}$ = 7.1 Hz, CH_2), 3.15 (t, 4H, $^3J_{HH}$ = 7.1 Hz, CH_2), 1.83–1.95 (m, 8H, CH_2). IR (cm^{-1}): 3326 s *ν*(O–H), 1643 m *ν*(C=N). Anal. Calcd. for $C_{10}H_{18}Cl_4N_2O_2Pt$: C, 22.4; H, 3.4; N, 5.2. Found: C, 22.3; H, 3.3; N, 5.4%.

Synthesis of [$PtCl_2$(*o*-OC_6H_4CH=NOH)$_2$] (**8**). A solution of complex **4** (0.021 g, 0.045 mmol) in chloroform (5 mL) was treated with *N*,*N*-dichlorotosylamide (0.010 g, 0.045 mmol) and the mixture left overnight at ambient temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (60 Å; Merck) with chloroform as the eluent to give pure complex **8** as a reddish-brown solid (R_f 0.62). Yield: 60 %.

^{1}H NMR ($CDCl_3$), δ (ppm): 10.86 (s, 2H, $^3J_{PtH}$ = 15.2 Hz, OH), 8.11 (s, 2H, $^3J_{PtH}$ = 40.0 Hz,–CH=N), 7.39 (ddd, 2H, ^{3}J = 7.7 Hz, ^{4}J = 1.5 Hz), 7.25 (dd, 2H, ^{3}J = 13.9 Hz, ^{4}J = 1.40 Hz), 7.01 (d, 2H, ^{3}J = 8.44 Hz), 6.76 (dd, 2H, ^{3}J = 7.12 Hz). IR (cm^{-1}): 3275 m ν(O–H), 3015 w ν(C_{sp2}–H), 1651 s ν(C=N), 1599 s, 1549 m ν(C_{Ar}=C_{Ar}), 346 w ν(Pt–Cl). HRMS (ESI^-), m/z: 535.9760 $[M–H]^-$ (calc. 535.9744). Anal. calcd. for $C_{14}H_{12}Cl_2N_2O_4Pt$: C, 31.2; H, 2.3; N, 5.2. Found: C, 30.7; H, 1.8; N, 5.2%.

X-ray crystal structure determinations

Crystals of complexes **1**, **6**, and **7** were immersed in cryo-oil, mounted in a nylon loop, and analysed at a temperature of 100 K. The X-ray diffraction data were collected on a Bruker Axs Smart Apex II or Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Apex2* [14] *or Denzo-Scalepack* [15] program packages were used for cell

refinements and data reductions. The structures were solved by direct methods using *SHELXS-97* [16] with the *WinGX* [17] graphical user interface. A semi-empirical absorption correction (*SADABS*) [18] was applied to all data. Structural refinements were carried out using *SHELXL-97 or Bruker SHELXTL* [16]. In all structures, the OH hydrogen atoms were located from the difference Fourier maps, but constrained to ride on their parent oxygen with $U_{iso} = 1.5 \cdot U_{eq}$ (parent atom). Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.99 Å and $U_{iso} = 1.2–1.5\ U_{eq}$(parent atom). The crystallographic details are summarized in Table 1.

Table 1 Crystal Data.

	1	**6**	**7**
empirical formula	$C_6H_{14}Cl_2N_2O_2Pt$	$C_4H_{10}Cl_4N_2O_2Pt$	$C_{10}H_{18}Cl_4N_2O_2Pt$
fw	412.18	455.03	535.15
temp (K)	100(2)	100(2)	100(2)
λ(Å)	0.71073	0.71073	0.71073
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	4.5083(2)	12.0890(3)	6.4314(7)
b (Å)	8.5087(3)	6.61410(10)	14.2483(15)
c (Å)	14.5045(5)	13.8331(3)	8.5805(9)
β (deg)	91.856(2)	91.571(2)	101.659(2)
V (Å^3)	556.10(4)	1105.65(4)	770.06(14)
Z	2	4	2
ρ_{calc} (Mg/m^3)	2.462	2.734	2.308
μ(Mo Kα) (mm^{-1})	13.069	13.628	9.802
No. reflns.	7453	18253	7554
Unique reflns.	2118	3013	2027
GOOF (F^2)	1.068	1.176	0.972
R_{int}	0.0267	0.0443	0.0316
R1[a] ($I \geq 2\sigma$)	0.0193	0.0240	0.0222
wR2[b] ($I \geq 2\sigma$)	0.0380	0.0525	0.0558

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

Results and discussion

The reactions of (oxime)Pt^{II} complexes with *N*,*N*-dichlorotosylamide were studied. *N*,*N*-Dichlorotosylamide was used as a solid source of "positive chlorine". To the best of our knowledge, this is the first example of use of *N*,*N*-dichlorotosylamide for selective oxidation of platinum(II) species; the only precedent being the application of *N*,*N*-dichlorobenzenesulfonamide for the oxidative chlorination of *trans*-[$PtCl_2$(HN=C(OMe)Et)$_2$] [7]. It is known that *N*,*N*-dichlorotosylamide is relatively reactive, but can nevertheless be easily handled [19]. In order to study the reactivity of *N*,*N*-dichlorotosylamide in the oxidative chlorination of (oxime)Pt^{II} complexes, we chose a series of coordination compounds with different oxime ligands, *i.e.* aldoximes (acetaldoxime and salicylaldoxime) and ketoximes (acetoxime and cyclopentanone oxime). The (oxime)Pt^{II} complexes were synthesized by the previously published reaction between $K_2[PtCl_4]$ and oximes in a 1:2 molar ratio in water. The prepared compounds were characterized by elemental analyses, HRMS (ESI), IR and ^{1}H NMR spectroscopies; complex **1** was also characterized by X-ray single-crystal diffraction (Fig. 1).

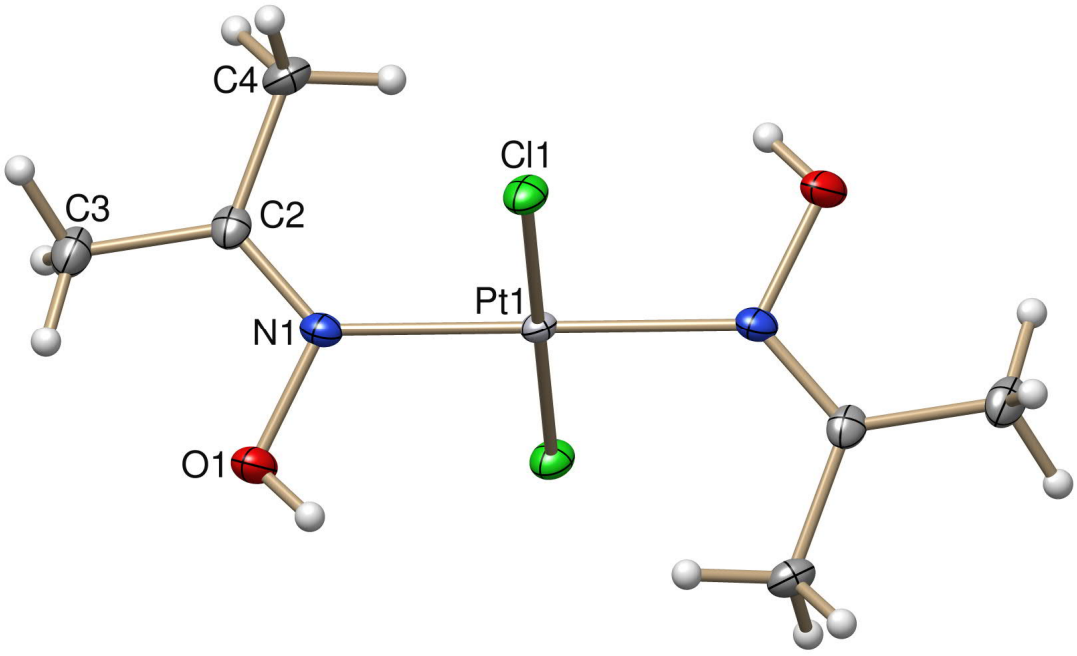


Fig. 1 Displacement ellipsoid plot of complex **1** at the 50% probability level (symmetry transformations used to generate equivalent non-labeled atoms: -x,-y+2,-z+2).

In complex **1**, each Pt atom has a centrosymmetric square-planar environment provided by two acetoxime N and two Cl atoms (Pt–N 2.008(2) Å, Pt–Cl 2.3019(6) Å, N–Pt–Cl 89.91(7)°) (Table 2). The N(1)–C(2) bond length in **1** (1.286(4) Å) is typical of N=C bonds in (oxime)Pt^{II} compounds. The O(1)–N(1)–Pt(1)–Cl(1) torsion angle is 67.38º. The structure of **1** displays column packing, which runs along the a-axis (Fig. 2). Owing to the $OH_{oxime}\cdots Cl$ hydrogen bonding (the H(1O)···Cl(1#) distance is 2.23 Å, whilst the O(1)–H(1O)···Cl(1#) angle is 164.4°), the *trans*-$[PtCl_2(acetoxime)_2]$ molecules are linked together into 1D arrays along the crystallographic a-axis.

Table 2 Selected bond lengths [Å] and angles [°] for **1**, **6**, and **7**.

	1	**6**	**7**
Pt(1)–N(1)	2.008(3)	2.030(3)	2.046(3)
Pt(1)–N(2)		2.041(3)	
Pt(1)–Cl(1)	2.3019(7)	2.3271(8)	2.3103(9)
Pt(1)–Cl(2)		2.3085(8)	2.3187(9)
Pt(1)–Cl(3)		2.3102(8)	
Pt(1)–Cl(4)		2.3240(8)	
N(1)–C(1)			1.281(5)
N(1)–C(2)	1.286(4)	1.273(5)	
N(2)–C(3)		1.266(5)	
O(1)–N(1)	1.404(3)	1.386(4)	1.401(4)
O(2)–N(2)		1.395(4)	
Cl(1)–Pt(1)–N(1)	89.91(7)	88.99(8)	92.25(9)
Cl(2)–Pt(1)–N(1)		92.30(9)	89.64(8)
Cl(3)–Pt(1)–N(1)		88.39(8)	
Cl(4)–Pt(1)–N(1)		89.46(9)	
Cl(1)–Pt(1)–Cl(3)		177.17(3)	
Cl(2)–Pt(1)–Cl(4)		177.75(3)	
N(1)–Pt(1)–N(2)		178.75(11)	

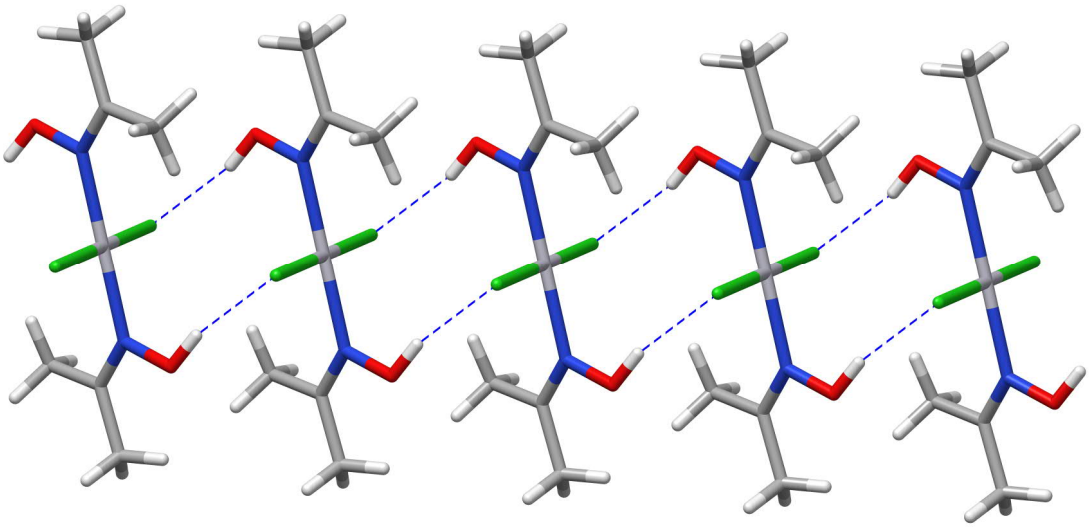
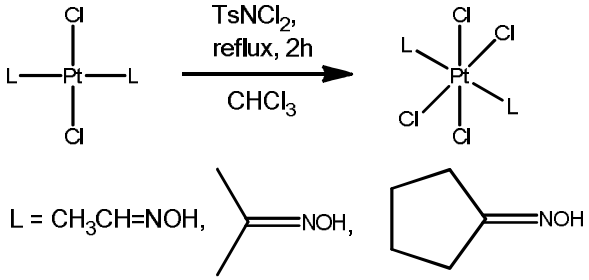


Fig. 2 Crystal packing of complex **1**.

Treatment of the *trans*-[$PtCl_2$(oxime)$_2$] complexes (where oxime = acetoxime, cyclopentanone oxime, or acetaldoxime) with *N*,*N*-dichlorotosylamide under identical conditions as used for the chlorination of [$PtCl_2$(imino ester)$_2$] [19] afforded *trans*-[$PtCl_4$(oxime)$_2$] (Scheme 3).



Scheme 3 Chlorination of the *trans*-[$PtCl_2$(oxime)$_2$] complexes by $TsNCl_2$.

In these reactions, a suspension of *trans*-[$PtCl_2$(oxime)$_2$] and *N*,*N*-dichlorotosylamide in a 1:1 molar ratio was refluxed for 2 h. As in the case of chlorination of *trans*-[$PtCl_2$(oxime)$_2$] (where oxime is acetoxime, cyclopentanone oxime, and acetaldoxime) by molecular chlorine, chlorination by *N*,*N*-dichlorotosylamide leads to the platinum(IV) complexes *trans*-[$PtCl_4$(oxime)$_2$]. Thus, only the oxidative chlorination of the platinum center is observed and the oxime

ligands remain unchanged. All our attempts to grow crystals of complex **5** suitable for single-crystal X-ray diffraction failed. However, crystals of good quality were obtained for complexes **6** and **7** by slow crystallization from chloroform.

In complex **6**, the platinum has a slightly distorted octahedral geometry with two axial acetaldoxime ligands and four chloride ligands (Fig. 3). The values of the Pt–Cl bond lengths agree well with those of previously characterized platinum(IV) chloride complexes, although all Pt–Cl bonds in complex **6** have different lengths due to the intramolecular interactions O(1)–H(1O)···Cl(4) (the H(1O)···Cl(4) distance is 2.29 Å, the O(1)–H(1O)···Cl(4) angle is 146.7°) and O(2)–H(2O)···Cl(1) (the H(2O)···Cl(1) distance is 2.28 Å, the O(2)–H(2O)···Cl(1) angle is 144.2°). The O(1)–N(1)–Pt(1)–Cl(4) and O(2)–N(2)–Pt(1)–Cl(1) torsion angles are 31.35 and 22.30°, respectively.

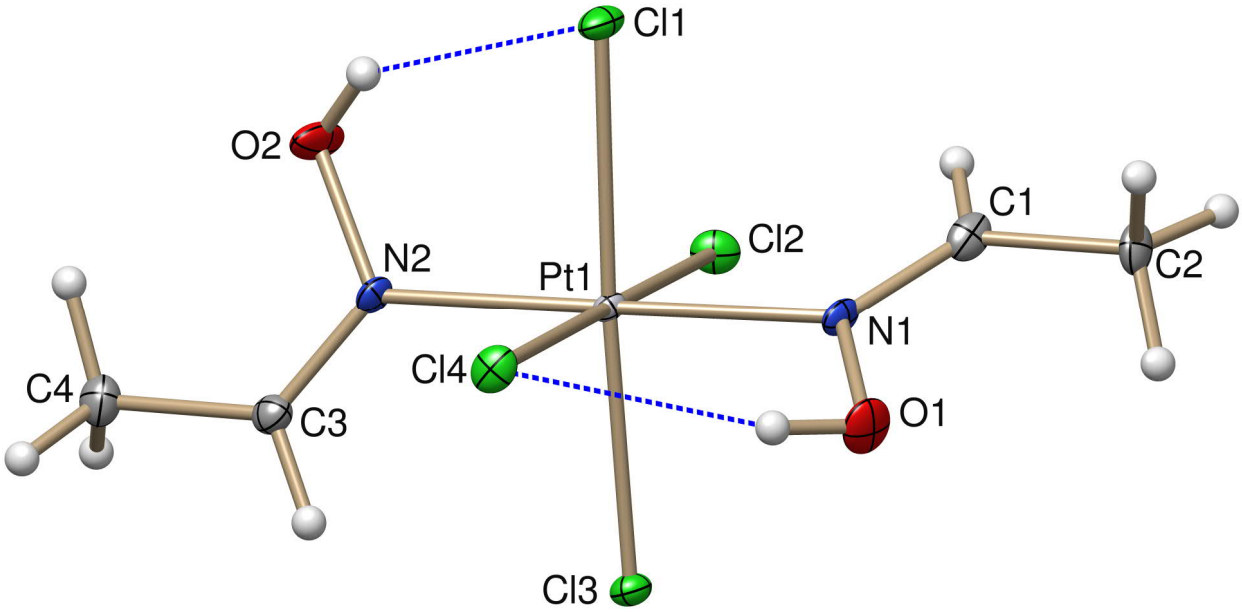


Fig. 3 Displacement ellipsoid plot of complex **6** at the 50% probability level.

In complex **7**, the coordination geometry of the platinum is octahedral (Fig. 4). The oxime ligands occupy the axial positions. The Pt–Cl(1), Pt–Cl(2), and Pt–N(1) bond lengths are 2.3103(9), 2.3187(9), and 2.046(3) Å, respectively. The crystal structure determination revealed the presence of intramolecular O(1)–H(1O)···Cl(1A) hydrogen bonds (the H(1O)···Cl(1A) distance is 2.36 Å, the O(1)–H(1O)···Cl(1A) angle is 130.1°). The O(1)–N(1)–Pt(1)–Cl(1A) torsion angle is 40.20°.

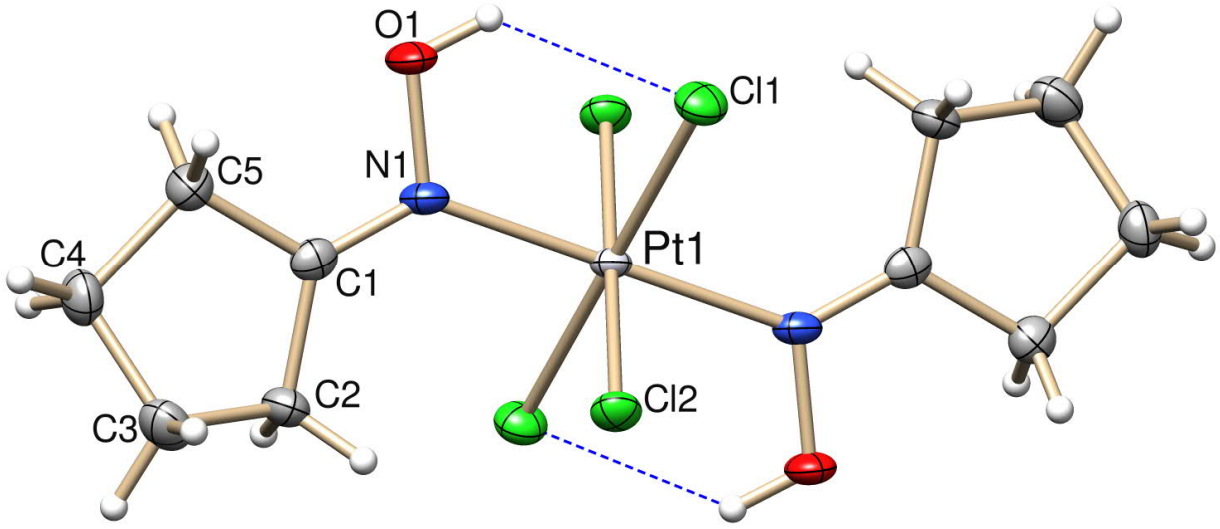


Fig. 4 Displacement ellipsoid plot of complex **7** at the 50% probability level (symmetry transformations used to generate equivalent non-labeled atoms: -x,-y,-z).

Chlorination of complex **4** under the same conditions as mentioned above leads to oxidation of the platinum center along with electrophilic substitution in the benzene rings. According to HRMS data, the reaction product has the formula $[PtCl_2(o\text{-}OC_6H_3ClCH{=}NOH)_2]$. However, when the reaction was carried out at room temperature only oxidation of Pt(II) to Pt(IV) was observed and the salicylaldoximato ligands remained intact (Scheme 2). Several attempts were made to obtain suitable crystals of complex **8** for X-ray diffraction studies. Unfortunately, crystals of sufficient quality could not be obtained. The reaction product was characterized by HRMS (ESI) and elemental analyses. Also, the infrared spectrum of this compound included a Pt–Cl band at 346 cm^{-1}. The ^1H NMR spectrum confirmed that electrophilic substitution in the benzene ring does not proceed.

Conclusions

In conclusion, the chlorination of (oxime)Pt^{II} (where oxime = aldoxime, cyclic or acyclic ketoxime) with *N*,*N*-dichlorotosylamide leads to selective oxidation of the Pt^{II} center, whereas the oxime ligands remain intact. The oxime ligands, which contain benzene rings activated to electrophilic substitution, do not react with $TsNCl_2$ under mild conditions. Furthermore, *N*,*N*-dichlorotosylamide can find a wide synthetic application in selective chlorination of the metal centers in the complexes, where the ligands may be easily subjected to electrophilic substitution processes.

Supplementary material

Crystal data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers CCDC 1041706, CCDC 1041705, and CCDC 1041612 for **1**, **6**, and **7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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