

PII: S0277-5387(98)00041-2

# Structure and reactivity of [PtX<sub>2</sub>(ketoxime)<sub>2</sub>] compounds. *Cis-trans* isomerization and X-ray structures of *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] and *trans*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] · 2MeC(=O)NMe<sub>2</sub>

Vadim Yu Kukushkin,<sup>a</sup>\*† David Tudela,<sup>a</sup>\* Youlia A. Izotova,<sup>a</sup>‡ Vitaly K. Belsky<sup>b</sup> and Adam I. Stash<sup>b</sup>

<sup>a</sup> Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>b</sup> L. Ya. Karpov Physico-Chemical Institute, Obukha Str. 10, 103064 Moscow, Russian Federation

(Received 17 November 1997; accepted 21 January 1998)

**Abstract**—The solid state thermal isomerization of *cis*-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] (X = Cl, ketoxime = Me<sub>2</sub>C=NOH, (CH<sub>2</sub>)<sub>4</sub>C = NOH, (CH<sub>2</sub>)<sub>5</sub>C=NOH; X = Br, ketoxime = Me<sub>2</sub>C=NOH) gives the corresponding *trans*-isomers in almost quantitative yields, thus showing that solid state isomerization is a general and convenient procedure for the synthesis of *trans*-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] complexes. X-ray structure analyses were performed for both *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] and the *bis*-dimethylacetamide solvate of *trans*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>]. The former compound crystallizes in the orthorhombic space group *Pbca* with *a* = 9.593(1), *b* = 14.827(2), *c* = 17.218(2) Å; *V* = 2449.0(8) Å<sup>3</sup>, *Z* = 8, and  $\rho_{calcd} = 2.718 \text{ cm}^{-3}$ . The latter complex crystallizes in the orthorhombic space group *Pbca* with *a* = 10.543(2), *b* = 17.676(4), *c* = 12.398(2) Å; *V* = 2310.5(8) Å<sup>3</sup>, *Z* = 4, and  $\rho_{calcd} = 1.941$  g cm<sup>-3</sup>. These two compounds are the first structurally characterized representatives of neutral Pt complexes with "simple" oximes. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: oximes; complexes of Pt(II) with oximes; cis-trans isomerization; crystal structure

Coordinated oxime ligands and oxime complexes display an impressively rich variety of reactivity modes which lead to unusual types of chemical compounds [1]. As far as the oxime chemistry of platinum is concerned, these complexes show a number of intriguing and little explored reactivity modes, e.g. oxidative coupling of two neighbouring oximes in Pt(IV) complexes [2,3], oxidation of oximes in Pt(II) complexes with the formation of nitrosoalkyl derivatives [4,5],

other ketones [4-6], addition of acetoxime to the allene ligand in a platinum(II) complex [7], oxime ligand supported stabilization of PtIII-PtIII derivatives [8], increasing of equilibrium acidity of oxime ligands on coordination [9], cyclometallation of oxime ligands in platinum(II) complexes [10], Pt(IV)-mediated hydrolysis of coordinated oxime ligand [11] and oxidation of Pt(II) complexes by 2-propanone oxime in concentrated hydrochloric acid [12]. Recently, two of us have reported self-assembly by hydrogen bonding in the ketoxime/ketoximato platinum(II) cis-[PtCl(Me<sub>2</sub>C=NO)(Me<sub>2</sub>C=NOH)<sub>2</sub>] complexes and  $[Pt(Me_2C=NO)_2(Me_2C=NOH)_2] \cdot 2H_2O$  [13]. Moreover, a novel type of hydrogen bonding, i.e. ( $\mu_4$ - $Cl^{-}$ ) · cis-[(···H-O)<sub>2</sub>(···H-CH<sub>2</sub>)<sub>2</sub>], has been observed [13]. These findings prompted us to inves-

addition of coordinated oximes to acetone and some

<sup>\*</sup> Authors to whom correspondence should be addressed.

<sup>†</sup>On sabbatical leave from Department of Chemistry, St Petersburg State University, 198904 Stary Petergof, Russian Federation.

<sup>‡</sup>On leave from St Petersburg Technological Institute, Zagorodny Pr. 49, 198013, St Petersburg, Russian Federation.

tigate more deeply both reactivity and other possible structural types of (ketoxime)platinum(II) complexes.

In spite of the fact that two cases of cis-trans rearrangement of [PtX<sub>2</sub>(ketoxime)<sub>2</sub>] have been documented [2,14], the general synthetic utility of solidstate isomerisation for the preparation of trans- $[PtX_2(ketoxime)_2]$  complexes had not been established, and no X-ray crystal structure of [PtX<sub>2</sub>(ketoxime)<sub>2</sub>] complexes had been published. We focused our attention on the cis-trans isomerization of  $[PtX_2(ketoxime)_2]$  for the following reasons: (i) these data are useful for the planned synthesis of the isomeric compounds, which display a very rich chemical reactivity [4–6], but had not been completely characterised; (ii) the geometrical isomerization should be taken into account in potential studies of biological activity, since in the vast majority of cases, the geometric isomers of [PtX<sub>2</sub>(amine)<sub>2</sub>] exhibit different structure-activity relationships [15–17]; (iii) the crystal structure of [Pt(Me<sub>2</sub>C=NOH)<sub>4</sub>]Cl<sub>2</sub> is suggestive of C—H  $\cdots$  Pt and C—H  $\cdots$  Cl interactions [13] that are similar to the so-called intermolecular multicenter hetero-acceptor (IMH) hydrogen bond [18], and it is interesting to study whether this kind of interaction is present in other Pt(II)-oxime complexes. In addition, there is current interest in the stacking of d<sup>8</sup>-ML<sub>4</sub> complexes [19].

In the course of this work we have determined the experimental conditions for the preparation of the isomeric pairs of  $[PtX_2(ketoxime)_2]$  (X = Cl, ketoxime =  $Me_2C = NOH$ ,  $(CH_2)_4C = NOH$ ,  $(CH_2)_5$ C=NOH; X = Br, ketoxime = Me<sub>2</sub>C=NOH), and solved the crystal structures of both cis-[PtBr<sub>2</sub>(Me<sub>2</sub> C=NOH)<sub>2</sub>] and the *bis*-dimethylacetamide solvate of trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>]. To the best of our knowledge these two compounds are the first structurally characterized representatives of neutral Pt complexes with so-called "simple" oximes-ligands which have merely one oxime group as the only coordination site—although the structures of [Pt(Me<sub>2</sub> C=NOH)<sub>4</sub>]Cl<sub>2</sub>[13] and some platinum(II) complexes with vic-dioxime ligands are known [19]. Previous attempts to solve the structure of cis-[PtCl<sub>2</sub>(Me<sub>2</sub> C=NOH)2], failed due to decomposition under Xray irradiation [2].

#### **EXPERIMENTAL**

#### Materials and instrumentation

The ketoxime ligands were purchased from Aldrich and used as received.  $K_2[PtCl_4]$  was obtained from Reakhim and recrystallized from water. All other chemicals and solvents were obtained from commercial sources and were used as received. Melting and/or decomposition points were determined in capillary. For TLC Riedel-deHaën 60 F 254 SiO<sub>2</sub>- plates with layer thickness 0.2 mm have been used. C, H and N elemental analyses were carried out by the Microanalytical Service, Universidad Autónoma de Madrid. EI mass-spectra were obtained with a VG Autospec instrument. Infrared spectra (4000–220 cm<sup>-1</sup>) were recorded on a Perkin–Elmer 1650 FT-IR spectrometer, using Nujol mulls between CsI windows. Raman spectra were measured on a Dilor XY spectrophotometer, using an Ar laser (5145 Å) with the powdered samples sealed in capillary tubes. <sup>1</sup>H NMR spectra were measured on a Bruker AMX-300 instrument.

## Synthetic work and characterization

Synthesis of cis- $[PtX_2(ketoxime)_2]$  compounds. The complexes cis- $[PtCl_2(ketoxime)_2]$  (ketoxime = Me<sub>2</sub>C=NOH, (CH<sub>2</sub>)<sub>4</sub>C=NOH, (CH<sub>2</sub>)<sub>5</sub>C=NOH) were prepared according to the published methods [2,20] from K<sub>2</sub>[PtCl<sub>4</sub>] and two equivalents of the appropriate oxime in water.

Synthesis of cis-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>]. (i) Starting from K<sub>2</sub>[PtCl<sub>4</sub>].—Potassium bromide (0.72 g, 6.0 mmol) is added to a solution of K<sub>2</sub>[PtCl<sub>4</sub>] (0.5 g, 1.2 mmol) in water (10 ml) and the mixture is left to stand at 20–25°C for 2 h. After addition of acetone oxime (0.18 g, 2.4 mmol), the reaction mixture is left to stand at the same temperature for 3 d, and the released crystals are filtered off and dried in air at 70°C. The yield of *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] is 0.35 g, 58% based on Pt.

(ii) Starting from *cis*-[PtCl<sub>2</sub>(Me<sub>2</sub>(C=NOH)<sub>2</sub>].— Solid silver nitrate (0.52 g, 3.1 mmol) is added during 10 min to a suspension of *cis*-[PtCl<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] (0.63 g, 1.5 mmol) in water (20 ml). After stirring the suspension for 4 h at room temperature, AgCl is filtered off and washed with water (5 ml). Potassium bromide (0.46 g, 3.8 mmol) is added to the pale-yellow filtrate, the reaction mixture is stirred for 15 min and a small amount of precipitate is filtered off. The yellow filtrate is left to stand for 12 h at room temperature, and prism-like crystals are collected on a filter and dried in air at 20–25°C. The yield of *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub> C=NOH)<sub>2</sub>] is 0.09 g. 11% based on Pt. Crystals suitable for X-ray analysis were grown directly from the reaction mass.

Yellow prisms from water, mp = 170°C. TLC on SiO<sub>2</sub>, MeCN: CHCl<sub>3</sub> = 2:1,  $R_f$  = 0.55. EI-MS, m/z: 500 (100%), 501 (75%) and 502 (95%) (M)<sup>+</sup>. Anal. Calcd for C<sub>6</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 14.4; H, 2.8; N, 5.6. Found: C, 14.7; H, 2.7; N, 5.7. IR data, cm<sup>-1</sup>: 1659 m-s v(C=N), 234 ms v(Pt—Br). Raman data, cm<sup>-1</sup>: 1661 m v(C=N), 234 s and 209 m v(Pt—Br). <sup>1</sup>H NMR in D<sub>2</sub>O,  $\delta$ , ppm : singlets at 2.18 and 2.64.  $J_{PtH}$  coupling constants are not well resolved.

Syntheses of trans-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] compounds. trans-[PtCl<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>], trans-[PtCl<sub>2</sub>{(CH<sub>2</sub>)<sub>n</sub> C=NOH}<sub>2</sub>] (n = 4, 5) and trans-[PtBr<sub>2</sub>(Me<sub>2</sub> C=NOH)<sub>2</sub>] were prepared by keeping the *cis*-isomers at 140°C for 4 h, 135°C for 6 h, 140°C for 6 h and 140°C for 5 h, respectively. In all cases the solid-state isomerization was monitored by TLC on SiO<sub>2</sub>. The properties of *trans*-[PtCl<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] have been described previously [2].

trans-[PtCl<sub>2</sub>{(CH<sub>2</sub>)<sub>4</sub>C==NOH}<sub>2</sub>]. This compound has no characteristic melting point. On slow heating in a capillary it decomposes from ca 190°C. EI-MS, m/z: 464 (70%) (M)<sup>+</sup>, 428 (15%) (M–HCl)<sup>+</sup>, 391 (100%) (M–2HCl)<sup>+</sup>, 361 (55%) (M–2HCl, -NO)<sup>+</sup>. TLC on SiO<sub>2</sub>, CHCl<sub>3</sub>: Me<sub>2</sub>CO = 6:1,  $R_f$ (trans) = 0.65, cf with  $R_f$ (cis) = 0.35 for the *cis*isomer. Anal. Calcd for C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 25.9; H, 3.9; N, 6.0. Found: C, 25.6; H, 3.9; N, 5.8. IR data, cm<sup>-1</sup>: 1668 ms  $v_{as}$ (C=N), 336 s  $v_{as}$ (Pt–Cl). Raman data, cm<sup>-1</sup> (decomposes in the laser beam): 330 w  $v_s$ (Pt–Cl). <sup>1</sup>H NMR in acetone- $d_6$ ,  $\delta$ , ppm: multiplets centered at 1.82 (8 H,  $\beta$ -CH<sub>2</sub>), 2.72 (4 H) and 3.09 (4 H) ( $\alpha$ -CH<sub>2</sub>), singlet at ca 10.0 (2 H, OH; very broad).

trans-[PtCl<sub>2</sub>{(CH<sub>2</sub>)<sub>5</sub>C=NOH}<sub>2</sub>]. The compound has no characteristic melting point. On slow heating in a capillary it decomposes from ca 190°C. EI-MS, m/z: 492 (55%) (M)<sup>+</sup>, 456 (15%) (M-HCl)<sup>+</sup>, 419 (100%) (M-2HCl)<sup>+</sup>, 389 (60%) (M-2HCl, -NO)<sup>+</sup>. TLC on SiO<sub>2</sub>, CHCl<sub>3</sub>: Me<sub>2</sub>CO = 6:1,  $R_f$ (trans) = 0.80, cf, with  $R_f$ (cis) = 0.45 for the *cis*isomer. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 29.3; H, 4.5; N, 5.7. Found: C, 29.5; H, 4.7; N, 5.7. IR data, cm<sup>-1</sup>: 1653 m  $v_{as}$ (C=N), 330 s  $v_{as}$ (Pt-Cl). Raman data, cm<sup>-1</sup> (decomposes in the laser beam): 325 w  $v_s$ (Pt-Cl). <sup>1</sup>H NMR in acetone- $d_6$ ,  $\delta$ , ppm: multiplets centered at 1.61 (4 H,  $\gamma$ -CH<sub>2</sub>), 1.81 (8 H,  $\beta$ -CH<sub>2</sub>), 2.71 (4 H) and 3.25 (4 H) ( $\alpha$ -CH<sub>2</sub>), singlet at 9.91 (2 H, OH; broad).

trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>]. Pale-yellow small crystals after recrystallization from boiling MeNO<sub>2</sub>,  $mp = 242-245^{\circ}C$ . TLC on  $SiO_2$ ,  $MeCN: CHCl_3 =$ 1:3,  $R_f = 0.60$ . EI-MS, m/z: 500 (100%), 501 (80%) and 502 (100%) (M)+. Anal. Calcd for C<sub>6</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 14.4; H, 2.8; N, 5.6. Found: C, 14.6; H, 2.5; N, 5.6. IR data, cm<sup>-1</sup>: 1667 m-s v(C=N), 246 s v(Pt-Br). <sup>1</sup>H NMR in acetone- $d_6$ ,  $\delta$ , ppm: singlets at 2.18 (6 (H), 2.60 (6 H) and 10.02 (2 H, broad).  $J_{PtH}$  coupling constants are not well resolved. Recrystallization of trans-[PtBr<sub>2</sub>(Me<sub>2</sub> C=NOH)<sub>2</sub>] from boiling dimethylacetamide gives the bis-solvate trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] · 2MeC(=O) NMe<sub>2</sub> as yellow crystals,  $mp = 140-143^{\circ}C$ . Anal. Calcd for C<sub>14</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>4</sub>Pt: C, 24.9; H, 4.8; N, 8.3. Found : C, 24.9; H, 4.3; N, 7.9. IR data, cm<sup>-1</sup>: 1614 vs, br. v(C==O), 244 s  $v_{as}(Pt=Br)$ . Raman data, cm<sup>-1</sup>: 1664 m  $v_s$  (C=N), 207 vs  $v_s$  (Pt-Br). The <sup>1</sup>H NMR spectrum in acetone- $d_6$  shows, in addition to the singlets corresponding to *trans*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] [2.18 (6 H), 2.61 (6 H) and 10.05 br (2 H) ppm], the singlets corresponding to MeC(=O)NMe<sub>2</sub> at  $\delta$ , ppm : 1.97 (6 H, MeC(=O)), 2.83 (6 H) and 3.00 (6 H)  $(NMe_2)$ .

X-ray structure determination of cis- $[PtBr_2(Me_2 C=NOH)_2]$  and trans- $[PtBr_2(Me_2 C=NOH)_2] \cdot 2Me$ C(=O)NMe<sub>2</sub> (data for the latter complex are given below in square brackets).

Diffraction data were collected on an Enraf-Nonius CAD-4 [Nicolet P3] diffractometer. Cell parameters for both complexes were obtained from 12 centred reflections with  $\theta$  between 10 and 12°, 2532 [1359] reflections were measured up to 50° by the  $\theta/2\theta$  scan technique. Three standard reflections were measured every 60 min and showed practically no change with time [in the case of the solvate [PtBr<sub>2</sub>(Me<sub>2</sub>C-=NOH)<sub>2</sub>·2MeC(=O)NMe<sub>2</sub>, the crystal was packed in Cyacrine glue to prevent decomposition, but crystal decay was 2%]. Diffractometer data were processed by the program PROFIT [21] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson synthesis using the SHELXTL package [22]. After that, all reflections with  $I < 2\sigma(I)$  were excluded from calculations. Refinement was done by full-matrix least squares based on  $F^2$  using the SHELX-93 package [23]. All non H-atoms were treated anisotropically. H-atom coordinates were found from difference syntheses and were included in refinement with fixed positional and thermal parameters. An extinction correction has been applied (x = 0.014 [0.015]) Lorentz, polarization and absorption corrections were made [24]. Scattering factors were obtained from the International Tables for X-ray Crystallography [25]. All important crystallographic and refinement parameters for both structures are summarized in Table 1, and bond distances and angles are collected in Tables 2 and 3. Tables of atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

### **RESULTS AND DISCUSSION**

The interest in processes of geometrical isomerization of platinum(II) complex [PtX<sub>2</sub>L<sub>2</sub>] (where X = halide or pseudohalide, L = N-donor ligand) is partly due to the anticancer activity of some  $[PtX_2L_2]$ compounds [15-17]. Additionally, these rearrangements are of synthetic utility for the preparation of the trans-isomers. A fairly large number of studies concerning the *cis-trans* conversion of  $[PtX_2L_2]$  $(L = NH_3 [26-28] and other ligands with sp^3 - [29-31],$ *sp*<sup>2</sup>- [32–34] and *sp*-hybridized *N*-donor atoms [35]) have been carried out, but very little is known about the cis-trans isomerization of ketoxime complexes  $[PtX_2(ketoxime)_2]$ . In continuation of a DTA/TG study [13], two of us recently observed that on heating cis-[PtCl<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] undergoes a cis-trans isomerization [2].

We report herein that the solid-state *cis-trans* rearrangement occurs in a similar way for the oxime

V. Y. Kukushkin et al.

Compound	cis-[PtBr <sub>2</sub> (Me <sub>2</sub> C=NOH) <sub>2</sub> ]	trans-[PtBr <sub>2</sub> (Me <sub>2</sub> C=NOH) <sub>2</sub> ]·2MeC(=O)NMe <sub>2</sub>
Empirical formula	$C_6H_{14}Br_2N_2O_2Pt$	$C_{14}H_{32}Br_2N_4O_4Pt$
Formula weight	501.1	675.4
Colour	yellow	yellow
Crystal size (mm)	$0.37 \times 0.28 \times 0.08$	$0.45 \times 0.40 \times 0.15$
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)
a (Å)	9.593(1)	10.543(2)
$b(\mathbf{\hat{A}})$	14.827(2)	17.676(4)
$c(\dot{A})$	17.218(2)	12.398(2)
$V(Å^3)$	2449.0(8)	2310.5(8)
Z	8	4
$\rho_c (\mathrm{g}  \mathrm{cm}^{-3})$	2.718	1.941
$T(\mathbf{K})$	293(2)	293(2)
Radiation, $\lambda(A)$	Mo-K <sub>n</sub> , 0.71073	Mo-K <sub>a</sub> , 0.71073
$\mu$ , mm <sup>-1</sup>	17.961	9.555
Diffractometer	CAD-4	Nicolet P3
$\theta$ range (°)	2.37-24.97	2.30-25.04
Index ranges	h = 0 - 11	h = 0 - 12
-	k = 0 - 16	k = 0-20
	l = 0 - 20	l = 0 - 14
No. of coll. reflens	2532	1359
No. of unique reflexs with $I \ge 2\sigma(I)$	1084	1052
Max, min transmission	0.245 and 0.017	0.232 and 0.028
Refined parameters	119	116
Goodness-of-Fit on $F^2$	1.099	1.074
$R^a$	0.028	0.034
$wR2^b$	0.079	0.089
Largest diff. peak and hole $(e^{A^{-3}})$	1.117 and -1.328	1.355 and -1.276

Table 1. Crystal data and structure refinement

 ${}^{a} R = \Sigma(|F_{o}| - |F_{c}|) / \Sigma |F_{o}|$  ${}^{b} wR2 = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w F_{o}^{4}]^{1/2}$ 

Table 2. Bond	lengths (Å) and	d angles (°) for a	eis-[PtBr2(Me2C=NOH	$)_{2}$

Bond lengths			
Pt—N(1)	2.022(12)	Pt—N(2)	2.042(11)
Pt— $Br(2)$	2.385(2)	Pt-Br(1)	2.393(2)
O(1)—N(1)	1.41(2)	O(2)—N(2)	1.42(2)
N(1)—C(2)	1.30(2)	N(2)—C(5)	1.27(2)
C(1)—C(2)	1.46(2)	C(2)—C(3)	1.47(2)
C(4)—C(5)	1.50(2)	C(5)—C(6)	1.48(2)
		Bond angles	
N(1)— $Pt$ — $N(2)$	90.6(5)	N(1)— $Pt$ — $Br($	(2) 178.8(3)
N(2)— $Pt$ — $Br(2)$	89.7(3)	N(1)— $Pt$ — $Br($	(1) 90.3(3)
N(2)— $Pt$ — $Br(1)$	176.9(3)	Br(2)—Pt—Br	(1) 89.43(8)
C(2)-N(1)-O(1)	113.6(12	2) $C(2)-N(1)-I$	Pt 130.8(10)
O(1)—N(1)—Pt	115.6(8)	C(5)—N(2)—O	D(2) 113.9(12)
C(5)—N(2)—Pt	131.8(11	) $O(2)-N(2)-l$	Pt 114.0(8)
N(1)-C(2)-C(1)	123(2)	N(1)—C(2)—C	C(3) 120.7(14)
C(1)-C(2)-C(3)	117(2)	N(2)—C(5)—C	C(6) 118.2(14)
N(2) - C(5) - C(4)	121(2)	C(6)—C(5)—C	C(4) 121.0(14)

$2MeC(=O)NMe_2$						
Bond lengths						
Pt—Br	2.419(2)	C(4)—C(5) 1	.49(2)			
Pr-N(1)	2.016(8)	O(2)—C(4) 1	.22(2)			
O(1) - N(1)	1.384(12)	N(2)—C(4) 1	.32(2)			
N(1) - C(1)	1.268(14)	N(2)—C(6) 1	.47(2)			
C(1)—C(2)	1.47(2)	N(2)—C(7) 1	.44(2)			
C(1)—C(3)	1.51(2)					
	Bon	d angles				
N(1)— $Pt$ — $N(1)'$	180.0	N(1)—Pt—Br	90.7(3)			
N(1)'—Pt—Br	89.3(3)	Br—Pt—Br'	180.0			
C(1) - N(1) - O(1)	113.1(9)	C(1) - N(1) - Pt	128.9(9)			
O(1)—N(1)—Pt	118.0(6)	C(4) - N(2) - C(7)	119.4(12)			
C(4) - N(2) - C(6)	122.9(14)	C(7) - N(2) - C(6)	117.5(13)			
N(1) - C(1) - C(2)	124.6(12)	N(1)-C(1)-C(3)	117.7(10)			
C(2) - C(1) - C(3)	117.7(10)	O(2) - C(4) - N(2)	121.2(14)			
O(2) - C(4) - C(5)	120.1(13)	N(2)—C(4)—C(5)	118.7(14)			

Table 3. Bond lengths (Å) and angles (°) for *trans*- $[PtBr_2(Me_2C=NOH)_2] \cdot 2MeC(=O)NMe_3$ 

Symmetry code: (') 1-x, -y, -z

complexes  $[PtX_2(ketoxime)_2]$  studied. In all these cases, heating the *cis*-isomers at 135–140°C for 4–6 h led to the corresponding *trans*- $[PtX_2(ketoxime)_2]$  with almost quantitative yields. The direction of the rearrangement agrees with that predicted by the thermal isomerization rule [36]. A similar behaviour has been observed for both octahedral platinum(IV) [37] and tin(IV) halide complexes [38,39].

An alternative method for preparation of trans-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] consists of prolonged refluxing of cis-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] in aqueous media in the presence of free ketoxime [20]. We have established that the procedure can be successfully applied for the synthesis of *trans*- $[PtX_2(Me_2C=NOH)_2]$  (X = Cl, Br) but it is not efficient for the other complexes with more bulky and hydrophobic oximes,  $[PtX_2(ketoxime)_2]$  $(X = Cl, ketoxime = (CH_2)_4C = NOH, (CH_2)_5C = N$ OH), probably due to the poorer solubility of the starting cis-isomers in water. Therefore, solid-state isomerisation is a general and convenient procedure synthesis of trans-[PtX<sub>2</sub>(ketoxime)<sub>2</sub>] for the complexes.

We have performed X-ray structure analyses for both cis-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] (1) and trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] · 2MeC(=O)NMe<sub>2</sub> (2). The centrosymmetric solvate 2 was obtained after recrystallization of trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] from boiling dimethylacetamide. In 1 and 2, two Br and two N atoms form a slightly distorted square-planar coordination polyhedron around the Pt atoms, as shown in Figs 1 and 2, with angles around the Pt atoms close to 90 and 180°. Two acetoxime ligands are in *cis*positions to each other in 1 and in *trans*-positions in 2, and in both cases the ligands are coordinated to Pt through their nitrogen atoms. As expected, the ligands are planar in both complexes, with maximum devi-



Fig. 1. View of *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] with atomic numbering.

ations from the least-square planes through PtO(1) N(1)C(1)C(2)C(3) [PtO(2)N(2)C(4)C(5)C(6)] in **1** and PtN(1)O(1)C (1)C(2)C(3) in **2** of -0.007 Å for N(1) [0.022 Å for N(2)] and -0.021 Å for O(1), respectively. The Pt—N interatomic distances [2.022(12) and 2.042(11) Å for **1** and 2.016(8) for **2**] are consistent with those found in [Pt(Me<sub>2</sub>C=NOH)<sub>4</sub>] Cl<sub>2</sub> [13]. In the case of oximato ligands the negative charge makes them better donors than oxime ligands, thus shortening the Pt—N distance. So, for *cis*-[PtCl(Me<sub>2</sub>C=NO)(Me<sub>2</sub>C=NOH)<sub>2</sub>], with two crystallographically independent molecules, the



Fig. 2. View of trans-[PtBr<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>]  $\cdot$  2MeC(=O) NMe<sub>2</sub> with atomic numbering.

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) Å) [13]. The C—N distances are also consistent with those previously reported for trans-[PdCl<sub>2</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] [40] and [Pt(Me<sub>2</sub>C-=NOH)<sub>4</sub>]Cl<sub>2</sub> [13]. In the solvate **2**, the OH group of the oxime ligand is involved in a strong intermolecular hydrogen bond with a molecule of dimethylacetamide. The  $O(1) \cdots O(2)$  distance, 2.62(2) Å, is in the range of strong hydrogen bonds [41], which agrees with the acidic character of acetoxime ligands coordinated to Pt(II) [42]. According to Gutmann's second bond length variation rule [43], we could expect the formation of the hydrogen bond should lead to a shortening of the N-O bond distance. Nevertheless, the shortening of the N-O bond distance in 2 as compared to the N-O distances in 1 is not significant in terms of the standard deviations. Indeed, the N-O bond distances for both 1 (1.41(2) and 1.42(2) Å) and 2 (1.384(12) Å), agree with those found in  $[Pt(Me_2)]$ C=NOH)<sub>4</sub>]Cl<sub>2</sub> (1.385(5)–1.401(5) Å) [13].

The Pt—Br bond lengths in the *cis*-complex **1** [2.393(2) and 2.385(2) Å] are shorter than in the *trans*isomer **2** (2.419(2) Å), and in both K<sub>2</sub>[PtBr<sub>4</sub>] (2.445(2) Å) [44] and Rb<sub>2</sub>[PtBr<sub>4</sub>]  $\cdot$ H<sub>2</sub>O (2.435(3) Å) [45], but agree well with the Pt—Br bond lengths (*trans* to N) in *cis*-[PtBr<sub>2</sub>(Me<sub>2</sub>SO)(MeC=N)] (Pt—Br *trans* to S are 2.427(2), 2.429(2) and Pt—Br *trans* to N are 2.397(2), 2.394(2) Å; data are given for two crystallographically independent molecules [46]). The difference in the Pt—Br interatomic distances for **1**, **2** and [PtBr<sub>4</sub>]<sup>2-</sup> complexes suggests that the groundstate *trans*-influence of acetoxime is smaller than that of the bromide ligand.

A qualitative theoretical study has found that  $\pi$ acidic ligands enhance the M ... M stacking interactions in square-planar d<sup>8</sup>-ML<sub>4</sub> complexes, and [Pt(vic-dioximato)<sub>2</sub>] complexes show columnar stacking with short (in the range 3.17–3.50 Å)  $Pt \cdots Pt$ distances [19]. In 1 and 2, however, the steric hindrance due to the bulky = CMe<sub>2</sub> moieties leads to dihedral angles between the ligand planes and the coordination plane of  $67.1^{\circ}$  and  $73.5^{\circ}$  for 1 and  $85.1^{\circ}$ for 2. This, in turn, prevents the square-planar complexes from stacking and gives rise to long Pt ··· Pt separations. Indeed, the shortest Pt ··· Pt distances are 5.364 Å in 1 and 8.137 Å in 2. Unfortunately, hydrogen atoms could not be refined in the presence of the heavy Pt and Br atoms, and nothing can be discussed about the possibility of  $O-H\cdots Br$ ,  $O-H\cdots Pt$ , C—H  $\cdots$  Pt and C—H  $\cdots$  Br interactions.

To the best of our knowledge, this study is the first one supported by X-ray diffraction for the occurrence of *cis-trans* isomerization in ketoxime  $[PtX_2(RR'C=NOH)_2]$  compounds.

Acknowledgements—The authors are grateful to the Spanish Dirección General de Investigación Científica y Técnica for financial support (Project PB93-0277) and the award of a sabbatical fellowship to V. Yu. Kukushkin (Grant SAB 94-0317). V. K. Belsky and V. Yu. Kukushkin thank the Russian Fund of Basic Research for the Grants 97-03-33776 and 97-03-33626a, respectively.

## REFERENCES

- Kukushkin, V. Yu., Tudela, D. and Pombeiro, A. J. L., *Coord. Chem. Rev.*, 1996, **156**, 333.
- Kukushkin, V. Yu., Belsky, V. K., Aleksandrova, E. A., Konovalov, V. E. and Kirakosyan, G. A., *Inorg. Chem.*, 1992, **31**, 3836.
- Kukushkin, V. Yu., Belsky, V. K., Konovalov, V. E., Aleksandrova, E. A. and Pankova, E. Yu., *Zh. Obsch. Khim.*, 1991, 61, 254.
- Kukushkin, V. Yu., Tudela, D., Izotova, Yu. A., Belsky, V. K. and Stash, A. I., *Inorg. Chem.*, 1996, 35, 4926.
- Kukushkin, V. Yu., Izotova, Yu. A. and Tudela, D., Zh. Obsch. Khim., 1995, 65, 1918.
- Kukushkin, V. Yu., Belsky, V. K. and Tudela, D., *Inorg. Chem.*, 1996, **35**, 510.
- Hutton, A. T., McEwan, D. M., Show, B. L. and Wilkinson, S. W., J. Chem. Soc., Dalton Trans., 1983, 2011.
- Baxter, L. A. M., Heath, G. A., Raptis, R. G. and Willis, A. C., J. Am. Chem. Soc., 1992, 114, 694.
- 9. Stetsenko, A. S. and Lipner, B. S., *Zh. Obsch. Khim.*, 1974, **44**, 2289 and references therein.
- Krooglyak, E. V., Kazankov, G. M., Kurzeev, S. A., Polyakov, V. A., Semenov, A. N. and Ryabov, A. D., *Inorg. Chem.*, 1996, **35**, 4804.
- 11. Bléaupré, P. W. and Holland, W. J., *Mikrochim. Acta*, 1983, **3**, 341.
- 12. Guedes da Silva, M. F. C., Izotova, Yu. A., Pombeiro, A. J. L. and Kukushkin, V. Yu., *Inorg. Chim. Acta*, in press.

- Kukushkin, V. Yu., Nishioka, T., Tudela, D., Isobe, K. and Kinoshita, I., *Inorg. Chem.*, 1997, 36, 6157.
- Kukushkin, Yu. N., Strelin, S. G., Byankina, L. S. and Bakhireva, S. I., *Zh. Neorg. Khim.*, 1977, 22, 1720.
- Farrell, N., Transition Metal Complexes as Drugs and Chemotherapeutic Agents. In Catalysis by Metal Complexes, Vol. 11, ed. B. R. James and R. Ugo. Reidel-Kluwer, Dordrecht, 1989.
- 16. Reedijk, J., Inorg. Chim. Acta, 1992, 198–200, 873.
- McAuliffe, C. A., Sharma, H. L. and Tinker, N. D. In *Chemistry of the Platinum Group Metals*; *Recent Developments*, ed. F. R. Hartley. Elsevier, Amsterdam, 1991, p. 546.
- Braga, D., Grepioni, F., Tedesco, E., Biradha, K. and Desiraju, G. R., *Organometallics*, 1997, 16, 1846.
- Aullón, G. and Alvarez, S., Chem. Eur. J., 1997, 3, 655.
- Chernyaev, I. I. (ed.), Synthesis of Complex Compounds of Platinum Group Metals (in Russian). Nauka Publishers, Moscow, 1964, pp. 58–60.
- 21. Strel'tsov, V. A. and Zavodnik, V. E., Kristallografia, 1989, 34, 1369.
- Sheldrick, G. M., SHELXTL User Manual, Rev.
  Nicolet XRD Corp., 1981.
- 23. Sheldrick, G. M., SHELX-93. University of Göttingen, Göttingen, Germany, 1993.
- 24. Axelrud, L. G., Grin, Yu. N., Zavalii, P. Yu., Pecharsky, V. K. and Fundamensky, V. S., CSDuniversal program package for single crystal and/or powder structure data treatment. *XII-th European Crystallographic Meeting*, Collected Abstracts. Moscow, August 1989, p. 155.
- 25. International Tables for X-ray Crystallography, Vol. IV. Kynoch Press, Birmingham, 1974.
- 26. Nikolaev, A. V., Dokl. AN SSSR, 1938, 20, 577.
- Zheligovskaya, N. N., Chernova, N. A., Kileev, R. G. and Spitsin, V. I., *Koord. Khim.*, 1983, 9, 666.
- 28. Roe, S. P., Hill, J. O. and Magel, R. J., *Inorg. Chim. Acta*, 1986, **115**, L15 and references therein.

- Bistrenina, V. I., Shebaldova, A. D. and Koblova, O. E., *Koord. Khim.*, 1985, **11**, 528.
- Faraglia, G., Sindellari, L. and Sitran, S., *Thermochim. Acta*, 1987, **115**, 229 and references therein.
- 31. Kong, P.-C. and Rochon, F.D., *Inorg. Chim.* Acta, 1984, **83**, 65.
- Yakovlev, K. I., Stetsenko, A. I., Mamelkina, I. Yu., Pogareva, V. G. and Shkurko, O. P., *Koord. Khim.*, 1986, **12**, 1373.
- 33. Kuduk-Jaworska, J., Pol. J. Chem., 1985, 59, 705.
- Kukushkin, Yu. N., Abdurakhmanov, R. O. and Kiseleva, N. P., *Zh. Neorg. Khim.*, 1986, **31**, 2175.
- 35. Svensson, P., Lövqvist, K., Kukushkin, V. Yu. and Oskarsson, Å., *Acta Chem. Scand.*, 1995, **49**, 72 and references therein.
- 36. Kukushkin, Yu. N., *Platinum Metals Review*, 1991, **35**, 28 and references therein.
- Kukushkin, V. Yu., Zh. Neorg. Khim., 1988, 33, 1905; Russ. J. Inorg. Chem. (Engl. Transl.), 1988, 33, 1085.
- Tudela, D., Tornero, J. D., Monge, A. and Sánchez-Herencia, A. J., *Inorg. Chem.*, 1993, 32, 3928.
- Tudela, D. and Tornero, J. D., *Inorg. Chim. Acta*, 1993, **214**, 197.
- Kaitano, Y., Kobori, K., Tanimura, M. and Kinoshita, Y., *Bull. Chem. Soc. Japan*, 1974, 47, 2969.
- Gilli, P., Bertolasi, V., Ferretti, V. and Gilli, G., J. Am. Chem. Soc., 1994, 116, 909.
- 42. Stetsenko, A. I. and Lipner, B. S., Zh. Obstch. Khim., 1974, 44, 2289.
- Linert, W. and Gutmann, V., Coord. Chem. Rev., 1992, 117, 159.
- 44. Kroening, R. F., Rush, R. M., Martin, D. S. and Clardy, J. C., *Inorg. Chem.*, 1974, **13**, 1366.
- 45. Rodek, E., Sterzel, W., Bartl, H. and Schuckmann, W., *Neues Jahrb. Mineral.*, *Monatsh.*, 1979, 277.
- Belsky, V. K., Konovalov, V. E., Kukushkin, V. Yu. and Moiseev, A. I., *Inorg. Chim. Acta*, 1990, 169, 101.