

Short Communication

Thermal *Cis* to *Trans* Isomerization of [PtCl₂(C₂H₅CN)₂] and Crystal Structures of the *cis*- and *trans*-Isomers

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Geometrical isomerization of square-planar complexes [PtX₂L₂] (where X = halide or pseudohalide, L = *N*-donor ligand) has been studied intensively.^{1–3} The interest in these processes is partly due to the anticancer activity for some of the [PtX₂L₂] compounds.^{4–6} A fairly large number of studies concerning the *cis*–*trans* rearrangement of [PtX₂L₂] (L = NH₃⁷ and other ligands with *sp*³-hybridized^{8–11} as well as *sp*²-hybridized *N*-donor atoms^{12–14}) have been carried out, but very little is known about *cis*–*trans* isomerization of [PtX₂(RCN)₂] with *sp*-hybridized *N*-donor nitrile ligands.^{15–17} Recently one of us observed that on melting, *cis*-[PtCl₂(RCN)₂] (R = Me, CH₂Ph, CH₂CO₂Et) undergoes a *cis* to *trans* rearrangement, and this reaction has been used for preparation of the *trans*-isomers.¹⁵

So far the isomerization of [PtCl₂(EtCN)₂] has not been studied. However, Golovnya *et al.*¹⁸ have reported a thermogram for *cis*-[PtCl₂(EtCN)₂] in which the DTA curve shows paired endo–exo peaks not accompanied by mass loss. Since such peaks are characteristic for *cis*–*trans* isomerization^{1–3} we assumed that *cis*-[PtCl₂(EtCN)₂] is also subject to a geometrical rearrangement.

We here report the syntheses, the conditions for the *cis* to *trans* conversion and the crystal structures of *cis*- and *trans*-[PtCl₂(EtCN)₂] as determined by X-ray single-crystal diffraction.

Synthesis and characterization of the isomers. *Cis*-[PtCl₂(EtCN)₂] was prepared in accordance with Lebedinsky's method.^{19,20} Anal.: Calc. for *cis*-[PtCl₂(EtCN)₂]: Cl 18.9%; Pt 51.9%. Found: Cl 18.9%; Pt 51.7%. ¹H NMR spectroscopy and thin-layer

chromatography (TLC) show that the compound obtained is in fact a ca. 6:1 mixture of the *cis*- and *trans*-isomers. TLC on SiO₂ Merck Kieselgel 60 F₂₅₄ plates gave the following results: *R*_f(*cis*) = 0.55 (larger spot), *R*_f(*trans*) = 0.82 [CHCl₃; (CH₃)₂CO = 1:1, in volume]. The melting point of the *cis*-isomer in a capillary is 112–114°C with subsequent crystallization of *trans*-[PtCl₂(EtCN)₂] from the melt. The newly formed solid melts at 179–182°C. DTA analysis, heating rate 2.5°C min⁻¹: 105°C, endopeak; 110°C, exopeak (lit.: 112°C, endopeak; 130°C, exopeak¹⁸). *Trans*-[PtCl₂(EtCN)₂] was synthesized by keeping the *cis*-isomer at 110–115°C for 5 h and recrystallizing from MeOH. Anal.: Calc. for *trans*-[PtCl₂(EtCN)₂]: Cl 18.9%; Pt 51.9%. Found: Cl 18.7%; Pt 51.8%. ¹H NMR spectrum of *cis*-

Table 1. Crystallographic data for *cis*- and *trans*-[PtCl₂(EtCN)₂]. Hydrogen atoms were not located and not included in the structure factor calculations.

	<i>cis</i> -[PtCl ₂ (EtCN) ₂]	<i>trans</i> -[PtCl ₂ (EtCN) ₂]
Formula weight	376.15	376.15
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.5195(5)	5.1359(6)
<i>b</i> /Å	9.5506(6)	9.3930(7)
<i>c</i> /Å	14.8293(11)	10.9410(9)
β/°	92.25(1)	98.05(1)
<i>V</i> /Å ³	1064.18(22)	522.60(16)
<i>Z</i>	4	2
<i>D</i> _{calc} /Mg m ⁻³	2.348	2.390
Crystal dimensions/mm	0.24 × 0.15 × 0.10	0.21 × 0.13 × 0.16
μ/mm ⁻¹	13.778	14.028
<i>h, k, l</i> Range	0–12, 0–15, ±11	±9, 0–12, 0–19
No. of measured reflections	2710	1776
No. of reflections used in the refinements [<i>I</i> > 3σ(<i>I</i>)]	1786	910
No. of parameters refined	95	52
<i>R</i>	0.057	0.064
<i>R</i> _w	0.064	0.084
Δρ _{max} /min	1.95/–3.09	1.89/–5.75

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Table 2. Atomic coordinates and equivalent isotropic temperature factor coefficients with e.s.d.s for *cis*- and *trans*-[PtCl₂(EtCN)₂].

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} /Å ^{2a}
<i>cis</i> -[PtCl ₂ (EtCN) ₂]				
Pt	0.2116(1)	0.38153(7)	0.50340	2.20(3)
Cl(1)	0.3117(9)	0.3304(6)	0.6455(4)	4.8(3)
Cl(2)	0.1158(7)	0.1586(5)	0.4837(3)	3.4(2)
N(1)	0.281(2)	0.575(2)	0.522(1)	2.8(3) ^b
N(2)	0.123(2)	0.427(2)	0.379(1)	3.1(7)
C(1)	0.331(3)	0.693(2)	0.532(1)	3(1)
C(2)	0.383(3)	0.834(2)	0.550(2)	4(1)
C(3)	0.450(4)	0.865(3)	0.640(2)	7(2)
C(4)	0.066(3)	0.445(2)	0.304(1)	3(1)
C(5)	-0.007(3)	0.458(2)	0.213(1)	4(1)
C(6)	-0.161(3)	0.359(3)	0.202(2)	6(1)
<i>trans</i> -[PtCl ₂ (EtCN) ₂]				
Pt	0	0	0	2.26(3)
Cl(1)	0.061(1)	0.2386(6)	-0.0252(5)	4.0(2)
N(1)	-0.231(3)	0.040(2)	0.124(2)	3.0(5)
C(1)	-0.366(4)	0.066(2)	0.195(2)	3.1(7)
C(2)	-0.534(4)	0.094(2)	0.283(2)	2.7(5)
C(3)	-0.649(5)	-0.048(2)	0.339(2)	3.6(7)

$$^a B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

^b This atom is refined isotropically. An anisotropic model gave unreasonable results.

[PtCl₂(EtCN)₂] in CD₂Cl₂ (99.6 + atom % D) δ, ppm: 1.41 [t, *J*_{HH} = 7.6 Hz, CH₃], 2.86 [q, *J*_{HH} = 7.6 Hz, CH₂].
¹H NMR spectrum of *trans*-[PtCl₂(EtCN)₂] in CD₂Cl₂ (99.6 + atom % D) δ, ppm: 1.38 [t, *J*_{HH} = 7.6 Hz, CH₃], 2.88 [q, *J*_{HH} = 7.6 Hz, CH₂].

X-Ray diffraction study. All data were collected on a Huber diffractometer at 25°C employing monochromated MoK_α radiation (λ = 0.7107 Å). Cell dimensions were ob-

Table 3. Bond distances (in Å) and angles (in °) with e.s.d.s for *cis*- and *trans*-[PtCl₂(EtCN)₂].

<i>cis</i> -[PtCl ₂ (EtCN) ₂]			
Pt–Cl(1)	2.263(5)	N(1)–Pt–N(2)	89.8(6)
Pt–Cl(2)	2.263(5)	N(1)–Pt–Cl(1)	177.0(5)
Pt–N(1)	1.94(2)	N(1)–Pt–Cl(2)	89.9(5)
Pt–N(2)	1.98(2)	N(2)–Pt–Cl(1)	89.6(5)
N(1)–C(1)	1.20(2)	N(2)–Pt–Cl(2)	179.5(5)
C(1)–C(2)	1.42(3)	Cl(1)–Pt–Cl(2)	90.6(2)
C(2)–C(3)	1.44(3)	Pt–N(1)–C(1)	177(2)
N(2)–C(4)	1.19(2)	N(1)–C(1)–C(2)	176(2)
C(4)–C(5)	1.44(3)	C(1)–C(2)–C(3)	117(2)
C(5)–C(6)	1.50(3)	Pt–N(2)–C(4)	175(2)
		N(2)–C(4)–C(5)	177(2)
		C(4)–C(5)–C(6)	108(2)
<i>trans</i> -[PtCl ₂ (EtCN) ₂]			
Pt–Cl	2.285(5)	N–Pt–Cl(1)	90.2(5)
Pt–N	1.96(2)	N–Pt–Cl(1)	89.8(5)
N–C(1)	1.14(2)	Pt–N–C(1)	178(2)
C(1)–C(2)	1.40(2)	N–C(1)–C(2)	178(2)
C(2)–C(3)	1.60(3)	C(1)–C(2)–C(3)	114(2)

tained from least-squares refinements of 70 (*cis*) and 49 (*trans*) θ-values, measured on the diffractometer in the ranges 9.9 < θ < 19.9° and 13.6 < θ < 22.5°, respectively. Absorption corrections were made according to Walker and Stuart²¹ for both compounds. The structures were solved by standard Patterson and difference Fourier methods and refined by full-matrix least-squares calculations employing MSC (Texsan) programs.²² Crystal data, details on the data collections and refinements are given in Table 1 and atomic parameters in Table 2.

Both compounds consist of mononuclear complexes, [PtCl₂(EtCN)₂] (Figs. 1a and 1b), stacked in columns along *a* (Figs. 2a and 2b). Selected interatomic distances and angles within the complexes are given in Table 3. The observed Pt–N distances are not significantly different. The Pt–Cl distances in the *cis*-compound, 2.263(5) Å, are

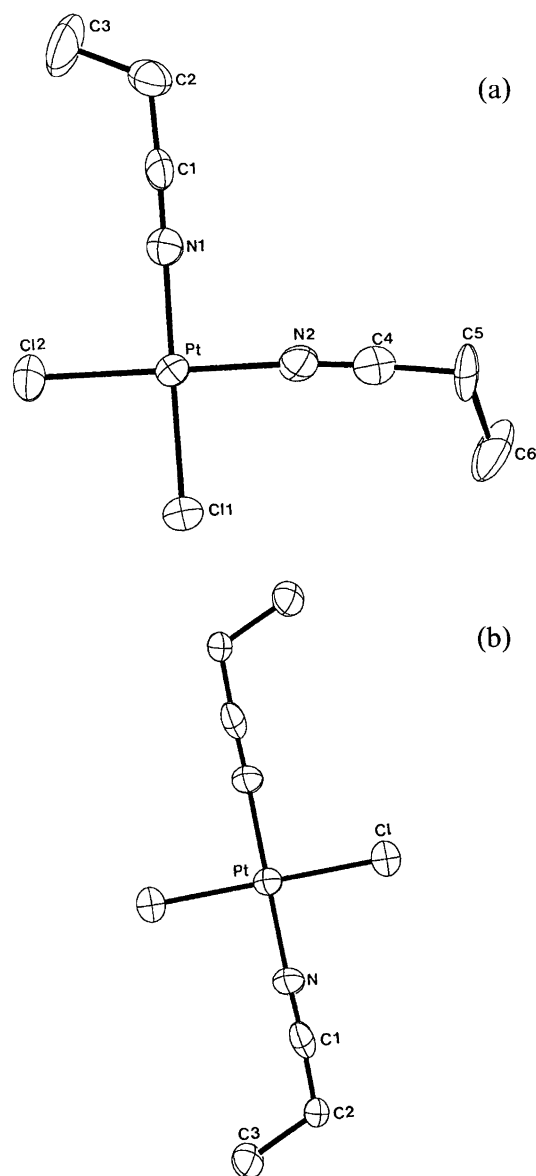


Fig. 1. Atomic numbering in the complexes (a) *cis*-[PtCl₂(EtCN)₂] and (b) *trans*-[PtCl₂(EtCN)₂].

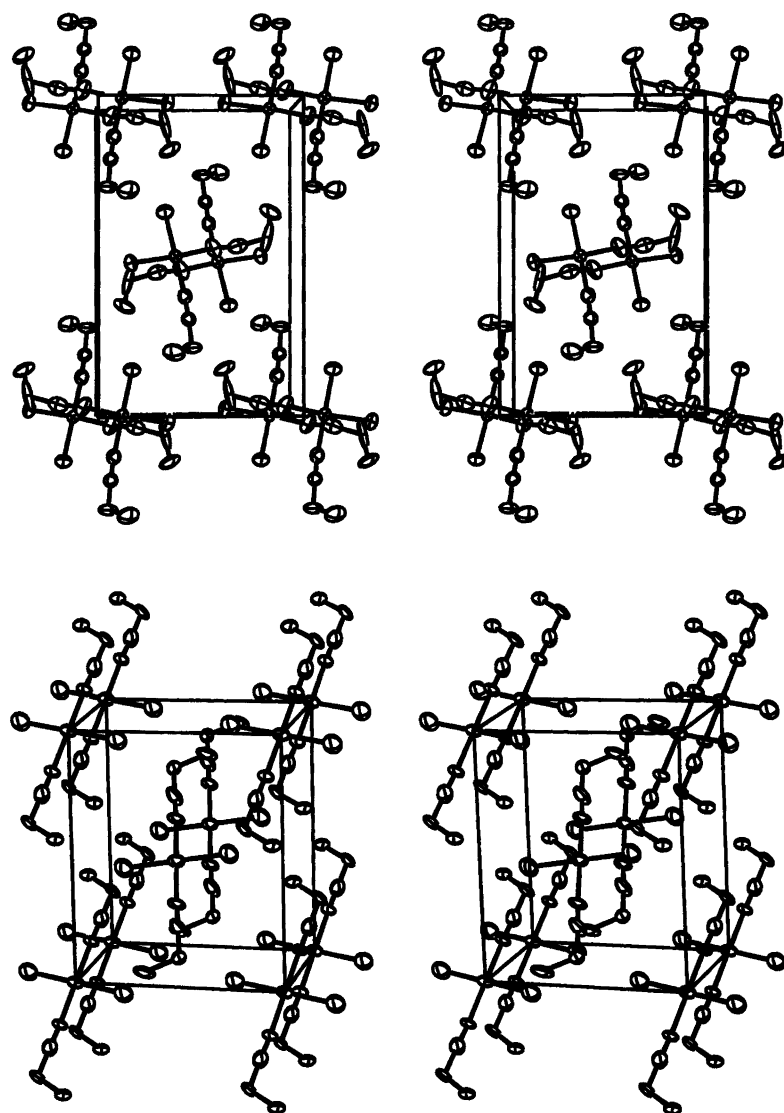


Fig. 2. Stereoscopic view of the crystal packing of (a) *cis*-[PtCl₂(EtCN)₂] and (b) *trans*-[PtCl₂(EtCN)₂].

on the other hand smaller than in the *trans*-compound, 2.285(5) Å, which most probably is due to a larger *trans*-influence of Cl as compared to N.

To our knowledge, this study is the first one supported by single-crystal X-ray diffraction for the occurrence of *cis*-to-*trans* isomerization in [PtCl₂(RCN)₂] nitrile compounds. It is also noteworthy that both isomers of [PtCl₂(EtCN)₂] are useful starting materials for Pt chemistry owing to their high solubility in common organic solvents and very good leaving properties of the coordinated nitriles. Various applications of *cis*- and *trans*-[PtCl₂(EtCN)₂] as synthetic intermediates are under current investigation in our group.²⁰

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