Crystal Structure of *trans*-Bis(acetonitrile)dichloroplatinum(II)

Jürgen Kritzenberger, Hartmut Yersin*

Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-93040 Regensburg

Klaus-Jürgen Range*, Manfred Zabel

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg

Z. Naturforsch. **49 b,** 297–300 (1994); received July 13, 1993

Crystal Structure, Absorption Data, *trans*-Bis(acetonitrile)dichloroplatinum(II)

We have determined the crystal and molecular structure of *trans*-bis(acetonitrile)dichloroplatinum(II). Crystallographic data for *trans*-$Pt(CH_3CN)_2Cl_2$: monoclinic, space group $P2_1/c$, $a = 5.0453(9)$, $b = 6.9896(5)$, $c = 11.962(1)$ Å, $\beta = 101.40(1)°$, $V = 413.5$ Å^3, $Z = 2$, $D_x = 2.796$ g cm^{-3}, $\mu(CuK\alpha) = 377.5$ cm^{-1}, $R = 0.0502$, $wR = 0.0529$ for 43 variables and 807 reflections with $F > 3\sigma(F)$. The Pt atom is in a planar configuration with N and Cl atoms in *trans* positions. The shortest distance between two Pt atoms corresponds to the length of the crystallographic *a*-axis (5.045 Å). Additionally, we present optical absorption data of the *cis*- and *trans*-isomer.

Introduction

cis-$Pt(CH_3CN)_2Cl_2$ was first prepared by Hoffmann and Bugge [1] and its configuration was verified by different groups [2, 3] through a crystal structure determination. Fanizzi *et al.* [4] reported the kinetics of the conversion of the *cis* to the *trans* isomer in a solution of acetonitrile. We have used this conversion to prepare single crystals of the *trans* compound by slow crystallization from a dilute solution of *cis*-$Pt(CH_3CN)_2Cl_2$. Main subject of this paper is the investigation of the crystal and molecular structure of *trans*-$Pt(CH_3CN)_2Cl_2$. Additionally we report on spectroscopic properties of both isomers.

Experimental

Cis-Bis(acetonitrile)dichloroplatinum(II) was prepared from K_2PtCl_4 (Degussa) and acetonitrile (Merck, >99.7%) according to the procedure of Hoffmann and Bugge [1]. Crystals of both isomers of good quality for X-ray structure analysis and spectroscopic investigations were obtained by evaporation of the solvent from acetonitrile solutions applying different conditions of crystal growth. Crystals of the *cis*-compound were prepared using a highly concentrated solution of *cis*-$Pt(CH_3CN)_2Cl_2$ after a few days at room temperature. The crystal type was checked using the Weissenberg technique. On the other hand, single crystals of *trans*-$Pt(CH_3CN)_2Cl_2$ were obtained by evaporation of the solvent of a solution of *cis*-$Pt(CH_3CN)_2Cl_2$ in a refrigerator at T = 6 °C over two months.

Elemental analysis was used to check the purity of the products. Analytical data calculated for $Pt(CH_3CN)_2Cl_2$: C, 13.8; N, 8.1; H, 1.7%. Found: *cis*-$Pt(CH_3CN)_2Cl_2$: C, 13.9; N, 8.0; H, 1.8%; *trans*-$Pt(CH_3CN)_2Cl_2$: C, 13.9; N, 8.0; H, 1.7%.

The crystal structure of *trans*-$Pt(CH_3CN)_2Cl_2$ was determined from a single crystal ($0.90 \times 0.14 \times 0.08$ mm) using an Enraf-Nonius CAD-4 diffractometer ($CuK\alpha$, $\lambda = 1.5418$ Å, graphite monochromator). Lattice parameters were refined from 2θ values of 18 reflections in the range $7° \leq 2\theta \leq 20°$. Systematic absence of reflections $h\,0\,l\,(l \neq 2n)$ and $0\,k\,0\,(k \neq 2n)$ indicated the centrosymmetric space group $P2_1/c$. Intensities were measured for $2° \leq 2\theta \leq 75°$ using the $\omega - 2\theta$ scan technique (scan width $0.50° + 0.15° \tan\theta$). Three standard reflections indicated a 3.9% loss of intensity (linearly corrected) during data collection. Merging of the 1312 collected intensities [$(\sin\theta_{max})/\lambda = 0.626$ Å^{-1}; $-6 \leq h \leq +6$, $-8 \leq k \leq +6$, $-15 \leq l \leq +11$] gave 807 unique reflections ($R_{int} = 0.043$) with $F > 3\sigma(F)$ which were considered observed, and these were used for the calculations with the program system SHELX-76 [5].

The structure was solved by the heavy-atom technique. The Pt atom was located from the three-dimensional Patterson map. The positions of all other atoms were obtained by difference Fourier calculations. Refinement of the atomic coordinates and isotropic temperature factors resulted in $wR =$

* Reprint requests to Prof. Dr. H. Yersin or to Prof. Dr. K.-J. Range.

Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen
0932–0776/94/0300–0297/$ 01.00/0

0.126. At this stage a numerical correction for absorption (program DIFABS [6]) (μ = 377.5 cm^{-1}) was applied before performing the final refinement (anisotropic for all atoms except H atoms, which were not located). Final $R = 0.0502$, $wR = 0.0529$, $w = 1/\sigma^2(F)$ for 834 absorption-corrected observed reflections. $(\Delta/\sigma)_{max} < 0.001$ in the final refinement cycle, 43 parameters. Maximum features in the final $\Delta\varrho$ map +1.94, −3.41 eÅ^{-3}. Atomic scattering factors and f′, f″ values are taken from International Tables for X-ray Crystallography [7].

Optical absorption spectra of the complexes dissolved in acetonitrile (Merck, uvasol) were recorded with an Uvikon 960 (Kontron Co.) spectrophotometer.

Results and Discussion

Structure

The unit cell of *trans*-Pt(CH_3CN)$_2Cl_2$ is shown in Fig. 1, the corresponding cell parameters are summarized in Table I. Final atomic coordinates and equivalent isotropic displacement factors are given in Table II. Bond distances and important angles are summarized in Table III, calculated using the program SADIAN [8]*.

The Pt atom is coordinated in a quasi square-planar configuration with N and Cl atoms in *trans*-positions (Fig. 1). All these atoms lie strictly in the same plane according to crystallographic symmetry requirements.

Table I. Crystal data for *trans*-Pt(CH_3CN)$_2Cl_2$.

M_r (g mol^{-1})	348.10
Space group	$P2_1/c$
a (Å)	5.0453(9)
b (Å)	6.9896(5)
c (Å)	11.962(1)
α (°)	90
β (°)	101.40(1)
γ (°)	90
V (Å^3)	413.5
Z	2
D_x (g cm^{-3})	2.796
μ(CuKα) (cm^{-1})	377.5
R	0.0502
wR	0.0529

* Lists of structure factors, bond distances and bond angles have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen. Copies may be obtained by quoting the depository number CSD 00000, the name of the authors and literature citation.

Table II. Atomic coordinates and isotropic displacement factors (Å^2)[a].

Atom	x	y	z	U_{eq}/U_{iso}[b]
Pt	0	1/2	1/2	0.0240(5)
Cl	0.9424(8)	0.2550(6)	0.6208(3)	0.0440(19)
N	0.2333(22)	0.3360(16)	0.4304(9)	0.0294(55)
C1	0.3647(27)	0.2349(19)	0.3881(12)	0.0296(67)
C2	0.5280(34)	0.1091(20)	0.3352(14)	0.0425(82)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits; [b] the equivalent isotropic U values for atoms refined anisotropically are defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Interatomic distances (Å) and bond angles (°)[a].

Bond distances			Bond angles	
Pt–Cl	2.296(4)	(×2)	N–Pt–N	180.0
Pt–N	1.944(10)	(×2)	Cl–Pt–Cl	180.0
			N–Pt–Cl	89.6(3)
			N–Pt–Cl	90.4(3)
N–C1	1.152(16)		Pt–N–C1	177.8(10)
C1–C2	1.434(19)		N–C1–C2	180.0(24)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

A comparison of bond lengths and angles with those of *cis*-Pt(CH_3CN)$_2Cl_2$ [2, 3] shows only slight deviations. In the *trans*-compound the Pt–Cl distance is ≈ 0.03 Å longer, whereas the Pt–N distance is ≈ 0.03 Å shorter. The bond angles N–Pt–Cl exhibit only small differences from 90° for both isomers (1° for the *cis*- and 0.4° for the *trans*-isomer, respectively). The shortest Pt–Pt distances are 5.180 Å for *cis*-Pt(CH_3CN)$_2Cl_2$ and 5.045 Å for *trans*-Pt(CH_3CN)$_2Cl_2$. For the *trans*-isomer the distance between two Pt atoms corresponds to the lengths of the *a*-axis.

Optical absorption

The absorption spectra of the *cis*- and *trans*-isomers dissolved in acetonitrile were recorded using concentrations between 10^{-5} and 10^{-2} mol l^{-1} (T ≈ 300 K). The half-life of the isomerization of *cis*-Pt(CH_3CN)$_2Cl_2$ into *trans*-Pt(CH_3CN)$_2Cl_2$ is ≈ 14 h [4]. Therefore, all spectra were recorded using freshly prepared solutions. The energy positions, halfwidths and ε-values of all observed absorption

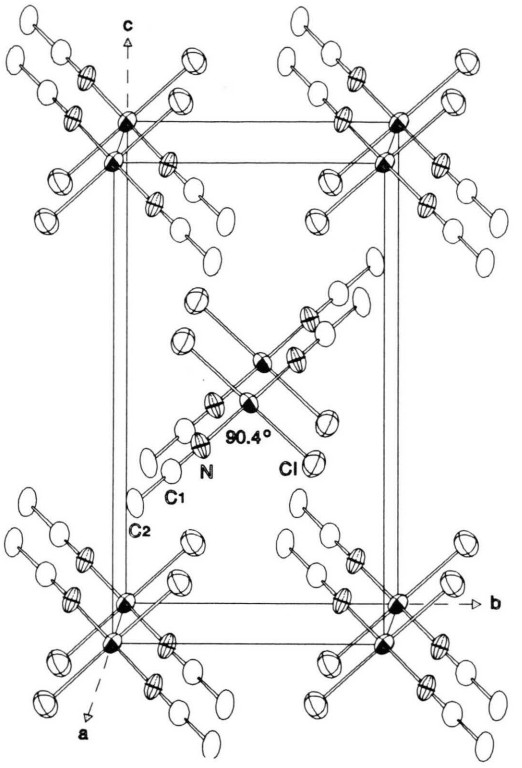

Fig. 1. ORTEP plot of the *trans*-$Pt(CH_3CN)_2Cl_2$ unit cell (protons are not shown).

bands are listed in Table IV. Reports on the electronic structure of diaminedichloroplatinum(II) are given in the literature [9, 10]. For $Pt(NH_3)_2Cl_2$ absorption bands at 45500 cm^{-1} (*cis*-isomer) and at 46500 cm^{-1} (*trans*-isomer) are both assigned to 5d → 6p transitions [9, 10]. If NH_3 is replaced by the CH_3CN ligand, like in $Pt(CH_3CN)_2Cl_2$, the π^* orbitals of the acetonitrile ligands will interact with a Pt 6p orbital, and this will lead to a red-shift of the LUMO. Thus, we expect an absorption with a high ε-value at lower energy than in $Pt(NH_3)_2Cl_2$ for both isomers. Indeed, the spectra exhibit an absorption at ≈ 42900 cm^{-1} (ε < 8000 l mol^{-1} cm^{-1}) for *cis*-$Pt(CH_3CN)_2Cl_2$ and at ≈ 43050 cm^{-1} (ε ≈ 4200 l mol^{-1} cm^{-1}) for *trans*-$Pt(CH_3CN)_2Cl_2$. Thus, we assign these absorption bands to (5d → 6p,π^*) transitions for both isomers. Absorption bands with $\bar{\nu}$ < 40000 cm^{-1} of $Pt(NH_3)_2Cl_2$ were assigned to d–d transitions [9, 10]. According to these results and to the observed ε-values of the absorption bands below 40000 cm^{-1} of *cis*- and *trans*-$Pt(CH_3CN)_2Cl_2$ (Table IV) we assign these transitions also to be

Table IV. Absorption bands[a] in *cis*- and *trans*-$Pt(CH_3CN)_2Cl_2$.

$\bar{\nu}_{max}$ [cm^{-1}]	ε [l mol^{-1} cm^{-1}]	halfwidth [cm^{-1}]
cis-$Pt(CH_3CN)_2Cl_2$		
22500	15[b]	2500
27300	40	4500
30600	150	4000
36350	260	3000
42900	8000	2200
44500	shoulder	
trans-$Pt(CH_3CN)_2Cl_2$		
23500	7[b]	2500
27000	15	3000
31150	50	3000
39800	250	1700
43050	4200	1300
44650	shoulder	

[a] Experimental errors: ± 100 cm^{-1} for energy positions and halfwidths and ± 10% for ε-values; [b] from single crystal absorption spectra using the crystallographic densities and the crystal thicknesses d [*cis*-isomer: 2.803 g cm^{-3} [2], d ≈ 6 μm; *trans*-isomer: 2.796 g cm^{-3} (Table I), d ≈ 10 μm]. All other values are from solution spectra.

mainly of 5d → 5d character. A comparison of the results of the *cis*- and the *trans*-isomer are an indication of the fact that transitions in systems with a center of inversion are symmetry forbidden. Thus, the ε-values of the d–d transitions are smaller for the *trans*-isomer.

Acknowlegement

We thank the DEGUSSA AG (Hanau) for a donation of $K_2[PtCl_4]$ and the Verband der Chemischen Industrie for financial support.

[1] K. A. Hoffmann, G. Bugge, Ber. **40,** 1772 (1907).
[2] F. D. Rochon, R. Melanson, H. E. Howard-Lock, C. J. L. Lock, G. Turner, Can. J. Chem. **62,** 860 (1984).
[3] G. R. Newkome, V. K. Gupta, F. R. Fronczek, Acta Crystallogr. **C 42,** 1643 (1986).
[4] F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, J. Chem. Soc. Dalton Trans. **1990,** 199.
[5] G. M. Sheldrick, SHELX-76. Program for Crystal Structure Determination. Univ. of Cambridge, England (1976).
[6] N. Walker, D. Stuart, Acta Crystallogr. **A 39,** 159 (1983).
[7] International Tables for X-ray Crystallography, Vol. IV, Kluwer Academic Publishers, Dordrecht, Birmingham: Kynoch Press (1974).
[8] W. H. Baur, G. Wenninger, SADIAN. Program for calculation of atomic distances and angles in crystal structures. Univ. of Illinois, USA (1969).
[9] H. H. Patterson, J. C. Tewksbury, M. Martin, M.-B. Krogh-Jespersen, J. A. LoMenzo, H. O. Hooper, A. K. Viswanath, Inorg. Chem. **20,** 2297 (1981).
[10] J. Chatt, G. A. Gamlen, L. E. Orgel, J. Chem. Soc. **1958,** 486.