Inorganica Chimica Acta, *111* (1986) L35–L37

Mechanism of Reaction of Zeise's Salt with β-Alanine. Crystal and Molecular Structure of *trans*-(N,olefin)-[Pt(C_2H_4)(β-alaninato)Cl]

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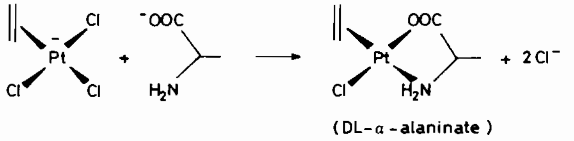
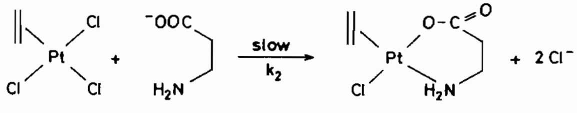
Received July 30, 1985

The stability of Pt(II) olefin complexes toward loss of the coordinated olefin is a matter of great current interest [1]. Recent studies in the field have shown that the presence of a positive charge in cationic complexes destabilizes the platinum–olefin bond [2]. Particularly interesting is the reaction of Zeise's salt with bidentate ligands, which may be halted before the Pt–olefin bond rupture by the use of anionic ligands, such as aminoacid anions [2c]:



We have now studied the kinetics and mechanism of such a reaction employing the anion of β-alanine, wherein the chelate Pt-containing ring bears one additional carbon atom.

The reaction



I Ala II

is second-order in substrate and bidentate ligand concentrations. Spectral changes are shown in Fig. 1. The rate law is of the form:

$k_{obs} = k_2[\text{Ala}]$

(under pseudo-first order conditions; the pH was kept constant with a phosphate buffer. Ionic strength = 0.2 M with $LiClO_4$). Activation parameters for the k_2 term are $\Delta H^{\ddagger} = 16 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger} = -15 \pm 3$ e.u. (see the Eyring plot in Fig. 2), in agreement with the bimolecular nature of the process.

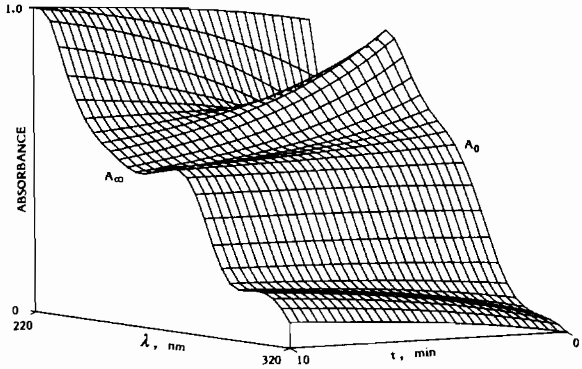


Fig. 1. 3D representation of spectral changes for the reaction of Zeise's salt with β-alaninato showing the dependence of absorbance with time from single exponential nonlinear regression of absorbance *vs.* time data.

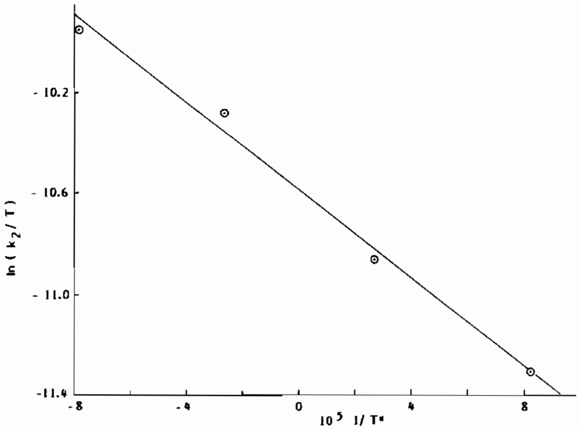
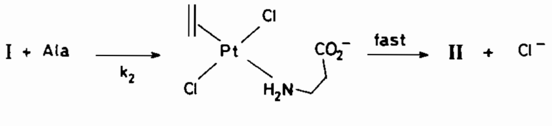


Fig. 2. Eyring plot of $\ln(k_2/T)$ data *vs.* $1/T^*$ where $1/T^* = 1/T - 1/T_0$ ($T_0 = 305.5$ K).

The following mechanism is proposed:



The ease of chelate ring closure with displacement of the *cis* chloride ligand is in agreement with the length of the $-CH_2-CH_2-$ chain in the β-amino-acid.

We have also carried out an X-ray analysis of the final complex **II** and determined its crystal and molecular structure, as described below.

0020-1693/86/$3.50

TABLE I. Atomic Parameters for $[PtCl(NH_2(CH_2)_2CO_2)(CH_2{=}CH_2)]$

(a) Fractional coordinates ($\times 10^4$) (M is the mid-point of the ethylene bond)

Atom	*x*	*y*	*z*
Pt	8830(1)	8022(1)	5521(1)
Cl	9639(9)	6944(9)	7996(10)
O(1)	8178(20)	9032(15)	3376(21)
O(2)	7075(19)	9226(17)	667(22)
N	9272(26)	6505(20)	4108(27)
C(1)	7641(26)	8554(25)	1854(32)
C(2)	7825(30)	7179(27)	1476(36)
C(3)	9136(32)	6619(29)	2346(39)
C(4)	8971(30)	9720(32)	6969(36)
C(5)	7693(40)	9336(33)	6747(39)
M	8332	9528	6858

(b) Anisotropic temperature factors ($\times 10^2$) in the form $T = \exp[-2\pi^2(\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	3.57(5)	2.92(5)	2.44(4)	0.48(4)	0.93(3)	−0.07(5)
Cl	7.8(6)	6.7(5)	3.5(4)	2.3(4)	2.3(4)	1.8(5)
O(1)	6.3(12)	2.1(8)	2.4(8)	−0.2(6)	1.3(8)	1.1(8)
O(2)	4.4(10)	3.3(9)	2.6(8)	0.2(7)	0.2(7)	0.8(9)
N	6.7(16)	2.6(10)	2.9(10)	0.2(8)	2.6(10)	−0.1(10)
C(1)	3.0(12)	3.6(13)	3.0(12)	0.4(10)	0.6(10)	0.2(10)
C(2)	4.8(16)	3.4(15)	3.5(14)	−0.6(12)	−0.4(12)	3.1(13)
C(3)	5.0(18)	4.7(17)	3.7(16)	0.4(12)	0.0(13)	0.2(11)
C(4)	3.9(15)	6.0(19)	2.8(14)	−1.5(13)	−0.8(11)	1.2(14)
C(5)	9.6(26)	5.5(20)	4.0(16)	0.2(14)	4.3(17)	3.4(19)

X-ray Data

Cell parameters for $[PdCl(NH_2(CH_2)_2CO_2)(CH_2{=}CH_2)]$ were determined by least-squares from 2θ values for 25 medium angle reflexions, measured on a four-circle diffractometer with Mo Kα radiation. Crystal data are: $C_5H_{10}ClNO_2Pt$, $F_w = 346.5$, $F(000) = 632$, monoclinic, space group $P2_1/n$, general positions $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, with $a = 10.367(5)$, $b = 10.739(5)$, $c = 7.960(5)$ Å, $\beta = 102.91(4)^\circ$, $V = 864$ Å^3; $D_c = 2.66$ g cm^{-3} for $Z = 4$, and μ (Mo Kα) = 187.8 cm^{-1}. A total of 2403 reflexions was recorded at room temperature up to $\theta = 25^\circ$ with the Mo Kα wavelength by the $\theta/2\theta$ scan. Of these, 1853 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations. The intensities were corrected for Lorentz polarization and for absorption [3]. No crystal deterioration was observed during irradiation.

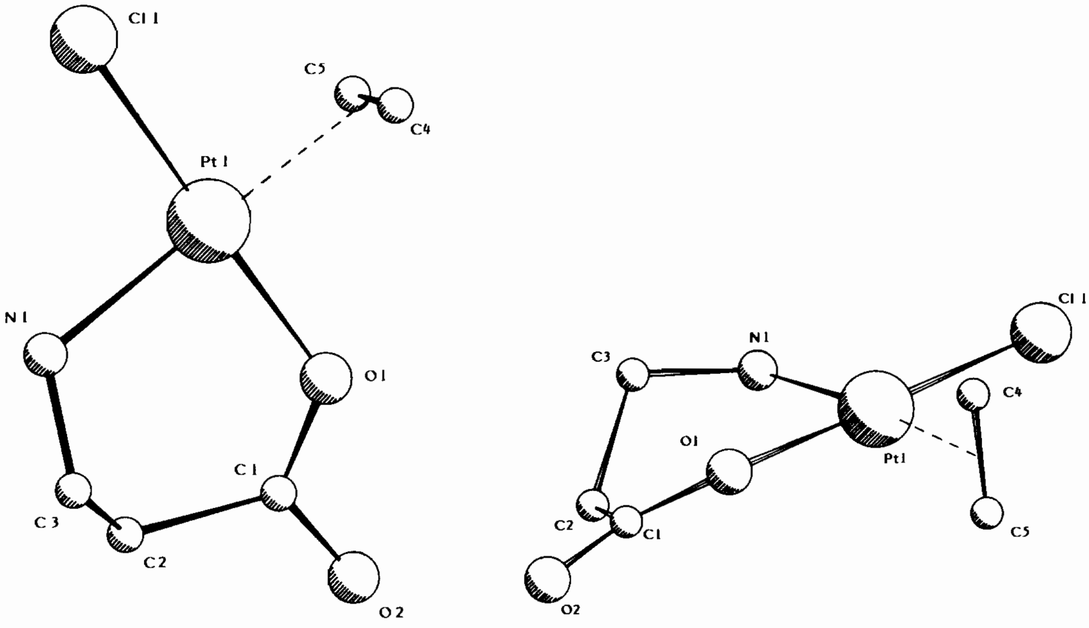
The structure was solved by standard methods and refined by least-squares. At convergence, the final *R* was 7.8%. Scattering factors for neutral atoms were those of ref. 10 for Pt, corrected for the anomalous dispersion; those for the other non-hydrogen atoms were supplied internally by SHELX [4].

Positional and thermal parameters are listed in Table I. Bond lengths and angles are given in Table II.

Description of the Structure

As shown in Fig. 3, the platinum atom is essentially square planar: the β-aminopropanoato anion is chelated through the amino nitrogen *trans* to the η-coordinated ethylene, and through the negatively charged oxygen of the carboxylato group *trans* to Cl. The coordination plane defined by Pt, Cl, N and O(1) contains the midpoint M of C(4)=C(5) and is described by the equation $-0.926\ x - 0.374\ y - 0.500\ z = -11.033$ Å with deviations Pt +0.03, Cl 0.00, N +0.04, O(1) −0.02, M +0.07 Å from the calculated mean plane. It is noteworthy that the direction of the ethylene double bond is only approximately perpendicular to the base plane, with an angle of 84°, and that the mid-point M is significantly displaced (by 0.07 Å) from this plane, which causes some asymmetry in the Pt–CH_2 separations.

Nevertheless, the Pt–M bond length of 2.06(3) Å between the platinum atom and the mid-point M is comparable with values in the range 2.04–2.06 Å



(a) (b)

Fig. 3. Structure of $[PtCl(H_2N(CH_2)_2CO_2)(CH_2{=}CH_2)]$.

TABLE II. Bond Parameters for $[PtCl(NH_2(CH_2)_2CO_2\text{-}(CH_2{=}CH_2)]$

(a) Bond distances[a] (Å)			
Pt–Cl	2.277(8)	C(1)–O(1)	1.32(3)
Pt–O(1)	2.01(1)	C(1)–O(2)	1.23(3)
Pt–N	2.09(2)	C(1)–C(2)	1.53(4)
Pt–C(4)	2.14(3)	C(2)–C(3)	1.51(4)
Pt–C(5)	2.20(3)	C(3)–N	1.38(3)
Pt–M	2.06(3)	C(4)–C(5)	1.36(5)
(b) Bond angles			
Cl–Pt–M	92.2(9)	O(1)–C(1)–O(2)	121(2)
O(1)–Pt–M	86.6(10)	C(2)–C(1)–O(2)	118(2)
Cl–Pt–N	89.2(6)	O(1)–C(1)–C(2)	121(2)
O(1)–Pt–N	92.1(7)	C(1)–C(2)–C(3)	116(2)
Pt–O(1)–C(1)	124(2)	C(2)–C(3)–N	112(3)
Pt–N–C(3)	120(2)		
Cl–Pt–O(1)	177.4(6)		
N–Pt–M	178.0(10)		
(c) Selected contact distances (Å)			
Cl···C(4)	3.13(3)	O(1)···C(5)	2.86(4)
Cl···C(5)	3.28(4)	O(1)···N	2.95(3)
O(1)···C(4)	2.89(3)	N···Cl	3.07(2)
Cl···M	3.13(4)		
O(1)···M	2.79(3)		

[a] M is the mid-point of the ethylene bond.

found in a series of platinum–olefin η-bonded compounds [5, 6].

The distances from Pt to the coordinated atoms are also in good agreement with available structure data for similar complexes [7–9]. As expected, the C–O(1) distance of 1.32 Å involving the charged oxygen atom is significantly long if compared with 1.23 Å of C=O(2), which is double in character.

The relatively close N···Cl contact distance of 3.07 Å suggests the possibility of intramolecular NH_2···Cl hydrogen bonding.

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