Inorganica Chimica Acta, 37 (1979) L545–L546
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A Bis-tetraalkyldiammonium Ion Bridging, *via* Carbon Bond, two Metal Atoms. X-ray Crystal Structure of Dichloro(3,3,6,6-tetramethyl-3,6-diazaoctane-1,8-diyl)bis(N,N,N′,N′-tetramethylethylenediamine)diplatinum(II) Diperchlorate

LUCIANA MARESCA, GIOVANNI NATILE*

Istituto di Chimica Generale ed Inorganica dell'Università, Calle Larga S. Marta 2137, 30123 Venice, Italy

ANTONIO TIRIPICCHIO, MARISA TIRIPICCHIO CAMELLINI

Istituto di Chimica Generale ed Inorganica and Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Università di Parma, via M. D'Azeglio 85, 43100 Parma, Italy

and GIUSEPPE RIZZARDI

Istituto di Chimica Generale ed Inorganica dell'Università, via Loredan 4, 35100 Padua, Italy

Received August 4, 1979

The five co-ordinate $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Me_4en)]$ complex [1], (*1*), reacts smoothly in methanol solution according to the following stoicheiometry:

$$3[Pt(C_2H_4)Cl_2(Me_4en)] \rightarrow [(Me_4en)ClPt–C_2H_4NMe_2C_2H_4NMe_2C_2H_4–PtCl–(Me_4en)]^{2+} + [Pt(C_2H_4)Cl_3]^- + Cl^- \qquad (1)$$

The dimeric cation $[Pt(Me_4en)ClPt–C_2H_4NMe_2C_2H_4NMe_2C_2H_4–PtCl–(Me_4en)]^{2+}$, (*2*), can be readily isolated as perchlorate salt and in this form is indefnitely stable at room temperature in the solid state, and can be recrystallized from hot methanol; however it reacts with stoicheiometric amount of aqueous mineral acids to give the cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)]^+$, (*3*), and the protonated diamine [2].

Complex (*3*) reacts with stoicheiometric amount of (*1*) to give again the dimeric cation (*2*) and Zeise's anion in quantitative yield (equation (2)).

$$2[Pt(C_2H_4)Cl(Me_4en)]^+ + Cl^- + [Pt(C_2H_4)Cl_2(Me_4en)] \rightarrow [(Me_4en)ClPt–C_2H_4NMe_2C_2H_4NMe_2C_2H_4–PtCl(Me_4en)]^{2+} + [Pt(C_2H_4)Cl_3]^- \quad (2)$$

This indicates that the decomposition of (*1*) in methanol occurs through an initial dissociation of a chloride ion to give (*3*) which, in turn, reacts with residual (*1*) to give (*2*).

The nucleophilic attack of amines on η^2-bonded ethene of neutral platinum(II) complexes has been largely studied in the past years. The η^1-ethene complexes which were formed had different stability depending upon the basicity and steric hindrance of the attacking amine, while secondary aliphatic amines gave quite stable adducts [2, 5], triethylamine did not react [6], and pyridines gave rise to equilibrium mixture of η^2- and η^1-ethene complexes [7]; in the latter case only pyridines bearing electron releasing substituents in *meta*- and *para*-position gave isolable η^1-adducts [8].

Therefore this is the first example in which nucleophilic attack of a tertiary aliphatic amine on η^2-bonded ethene is observed. Moreover, in our preparative conditions this reaction takes place even if the diamine is already coordinated to a metal atom (equation (2)) or if one end of it is already quaternized.

In order to confirm the proposed structure we performed an X-ray crystal structure of (*2*) as perchlorate salt.

TABLE I. Atomic Fractional Coordinates (× 10^4).

	x/a	*y/b*	*z/c*
Pt	7740(1)	4086(1)	3304(1)
Cl(1)	7694(7)	3346(5)	4929(6)
Cl(2)	2376(5)	3875(4)	1685(4)
O(1)	2187(22)	4421(20)	2600(19)
O(2)	3472(17)	4043(19)	1669(19)
O(3)	1391(19)	4284(21)	771(19)
O(4)	2400(29)	2901(20)	2050(27)
N(1)	5289(11)	6140(10)	4116(12)
N(2)	9283(12)	3269(12)	3436(13)
N(3)	7859(13)	4720(10)	1852(12)
C(1)	6221(14)	4794(14)	3123(15)
C(2)	6420(13)	5696(14)	3986(14)
C(3)	4608(14)	5273(14)	4451(15)
C(4)	5651(18)	7013(15)	4995(18)
C(5)	4483(17)	6592(16)	3002(17)
C(6)	9434(19)	3407(18)	2337(19)
C(7)	9088(19)	4515(18)	1907(19)
C(8)	9210(20)	2091(16)	3608(21)
C(9)	10300(18)	3688(20)	4353(20)
C(10)	7751(21)	5926(17)	1858(20)
C(11)	6934(22)	4313(20)	823(17)

Crystal Data

Crystals are monoclinic, space group $P2_1/c$ (from systematic absences), with a = 12.278(8), b = 12.681(9), c = 12.694(9) Å, β = 111.42(8)°; U = 1840 Å^3,

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*Author to whom correspondence should be addressed.

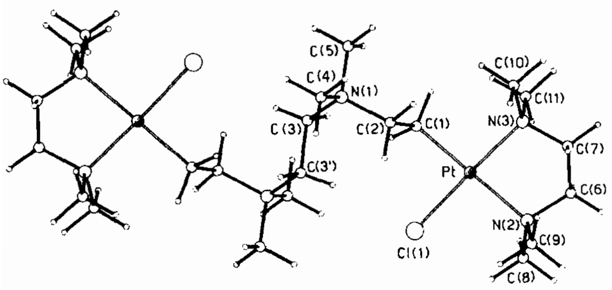

Fig. 1. The molecular structure of $[(Me_4en)ClPt-C_2H_4-NMe_2C_2H_4NMe_2C_2H_4-PtCl(Me_4en)]^{2+}$.

$Z = 2, M = 1064.7, D_c = 1.922$ g cm^{-3}. The intensities were measured in the $\theta-2\theta$ scan mode using Zr-filtered Mo-K$_\alpha$ radiation (μ = 173.2 cm^{-1}) on a Siemens on-line single crystal diffractometer. 3505 independent reflections were collected ($3 < \theta < 26°$) of which 2645 having $I > 2\sigma(I)$ were used in the analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares [10]. The hydrogen atoms were placed in their geometrically calculated positions and introduced in the final structure factors calculation but not refined; the final R was 0.049. The final atomic coordinates for the non-hydrogen atoms are given in Table I.

The molecular structure is shown in Fig. 1, bond distances and angles not involving the hydrogen atoms are reported in Table II. The molecule is centrosymmetric with a tetraalkyldiammonium ion bridging *via* an eight-member organic chain two platinum atoms; the co-ordination around each platinum is completed by a chlorine atom and a chelating Me$_4$en ligand. The Pt–N(2) and Pt–N(3) distances are significantly different revealing the different *trans* influence of Cl$^-$ and of an alkyl group.

TABLE II. Bond Distances (Å) and Angles (°) not involving Hydrogen Atoms with e.s.d.'s in Parentheses.

In the Pt co-ordination polyhedron			
Pt–Cl(1)	2.286(8)	Pt–N(3)	2.064(15)
Pt–N(2)	2.112(16)	Pt–C(1)	2.006(19)
Cl(1)–Pt–N(2)	92.5(5)	N(2)–Pt–N(3)	84.7(6)
Cl(1)–Pt–N(3)	177.2(5)	N(2)–Pt–C(1)	176.7(7)
Cl(1)–Pt–C(1)	87.6(6)	N(3)–Pt–C(1)	95.1(7)
In the organic ligand			
C(1)–C(2)	1.540(25)	N(2)–C(8)	1.517(26)
N(1)–C(2)	1.562(23)	N(2)–C(9)	1.461(29)
N(1)–C(3)	1.533(23)	C(6)–C(7)	1.511(32)
N(1)–C(4)	1.519(24)	N(3)–C(7)	1.508(30)
N(1)–C(5)	1.512(25)	N(3)–C(10)	1.535(25)
C(3)–$C(3^i)$	1.539(25)	N(3)–C(11)	1.476(27)
N(2)–C(6)	1.483(28)		
Pt–C(1)–C(2)	110.6(1.2)	C(8)–N(2)–C(9)	108.8(1.7)
N(1)–C(2)–C(1)	115.3(1.4)	C(8)–N(2)–Pt	113.3(1.3)
C(2)–N(1)–C(3)	111.5(1.2)	C(9)–N(2)–Pt	111.5(1.3)
C(2)–N(1)–C(4)	107.9(1.4)	C(10)–N(3)–C(11)	108.2(1.6)
C(2)–N(1)–C(5)	110.0(1.4)	C(10)–N(3)–Pt	110.4(1.2)
C(3)–N(1)–C(4)	111.2(1.4)	C(11)–N(3)–Pt	111.8(1.3)
C(3)–N(1)–C(5)	107.1(1.4)	C(10)–N(3)–C(7)	105.0(1.6)
C(4)–N(1)–C(5)	109.1(1.4)	C(11)–N(3)–C(7)	114.5(1.7)
N(1)–C(3)–$C(3^i)$	110.5(1.4)	C(7)–N(3)–Pt	106.7(1.1)
C(6)–N(2)–Pt	106.5(1.2)	C(7)–C(6)–N(2)	109.5(1.8)
C(6)–N(2)–C(8)	106.6(1.6)	C(6)–C(7)–N(3)	108.8(1.8)
C(6)–N(2)–C(9)	110.0(1.7)		
In the perchlorate ion			
Cl(2)–O(1)	1.442(25)	Cl(2)–O(3)	1.433(24)
Cl(2)–O(2)	1.370(24)	Cl(2)–O(4)	1.316(27)
O(1)–Cl(2)–O(2)	112.7(1.5)	O(2)–Cl(2)–O(3)	118.4(1.4)
O(1)–Cl(2)–O(3)	98.2(1.5)	O(2)–Cl(2)–O(4)	104.8(2.0)
O(1)–Cl(2)–O(4)	99.0(1.8)	O(3)–Cl(2)–O(4)	121.9(1.9)

$i = -x, -y, -z$

Acknowledgments

The authors are grateful to Consiglio Nazionale delle Ricerche (C.N.R.), Rome, for financial support.

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