Inorganica Chimica Acta, 132 (1987) 165–166

The Characterization of a Ring-opened Diethylenetriamine Complex of Pt(II). The Crystal Structure of Pt(dien·HCl)Cl$_2$

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(Received March 30, 1987)

Diethylenetriamine (dien) and substituted dien complexes of Pd(II) and Pt(II) represent ideal systems to study the substitution behaviour of the fourth coordination site. Most of our studies in the past have all emphasized the stability of the tridentate character of these dien ligands in such complexes [1–3]. However, in one study [4], indirect evidence for the isolation of a ring-opened complex, Pd(1,4,7-Me$_3$dien)Cl$_2$·HCl, was presented. In this species the dien ligand was suggested to be coordinated in a bidentate way with a protonated ring-opened amine group not attached to the metal center. We were unable to grow crystals suitable for a structure analysis, since this labile species ring-closes rapidly on dissolution to produce Pd(Me$_3$dien)Cl$^+$, which is accompanied by the release of HCl (1:1). Very recently we found complete loss of the dien ligand in Pd(1,1,7,7-Et$_4$dien)SO$_3$ at pH $<$ 6 due to the labilizing effect of coordinated sulfite [5]. These results have stimulated us to search for systems in which it is possible to isolate a stable ring-opened dien complex.

We succeeded in isolating a Pt(II) complex, Pt(dien)Cl$_2$·HCl, that was stable enough in aqueous solution to enable the successful isolation of crystals suitable for a structure analysis. The results confirmed our earlier reported [6] indirect evidence for a ring-opened dien species which is significantly more stable in aqueous solution than the related Pd(II) species due to the strength of the Pt–Cl bond.

Experimental

Pt(dien)Cl$_2$·HCl was prepared and characterized as described before [6]. Crystals were grown from a 1 M HCl solution of the complex.

TABLE I. Atomic Coordinates (X10^4) (e.s.d.s in parentheses)

	x	y	z
Pt	4010.8(5)	6836.7(5)	7611.3(5)
N1	2940(12)	6218(11)	8778(12)
C1	2713(16)	4857(14)	8565(15)
C2	2253(15)	4635(13)	6957(15)
N2	3375(12)	5176(10)	6511(11)
C3	2983(15)	5146(13)	4924(15)
C4	1790(16)	6071(15)	4179(14)
N3	1526(13)	6090(12)	2570(12)
Cl1	4771.3(4)	8566.0(3)	9062.0(4)
Cl2	5122.2(5)	7488.4(4)	6186.1(4)
Cl3	4251.9(3)	6814.0(4)	2188.6(3)

Structure analysis: the light yellow compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.548(2)$, $b = 10.474(1)$, $c = 10.135(1)$ Å, $\beta = 113.55(1)°$, $Z = 4$, $D_{\text{exp}} = 2.55$ and $D_{\text{calc}} = 2.563$ g cm^{-3}. The three dimensional intensity data were collected for θ values between 3° and 30° on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation. A crystal with dimensions 0.14 X 0.15 X 0.08 mm was used for the data collection. No decomposition of the crystal was detected during the data collection. A total of 3191 reflections were measured of which 2702 were considered as observed ($I > 3\sigma(I)$). The data were corrected for Lorentz, polarization and absorption effects.

The structure was solved by means of Patterson and Fourier methods. The final R value was 0.052 using all the observed reflections and anisotropic thermal parameters for all the non-hydrogen atoms. The final positional parameters with their estimated standard deviations are listed in Table I. See also 'Supplementary Material'.

Results and Discussion

This study nicely demonstrates that the isolation and existence of ring-opened bidentate dien complexes strongly depend on the stability of the metal–ligand bonds. These are known to be significantly stronger in the case of Pt(II) complexes as compared to Pd(II) complexes. In addition the pH of the solution plays an important role in stabilizing such ring-opened species via protonation of the uncoordinated ligand moiety.

The numbering scheme of the atoms in the [Pt(dienH)Cl$_2$]$^+$ cation is shown in Fig. 1 while the bond lengths and angles in the cation are given in Table II. The structure consists of discrete [Pt(dienH)Cl$_2$]$^+$ cations and chloride anions. The Cl$^-$ ion is surrounded by four nitrogen atoms (N1, N2 and 2 X N3)

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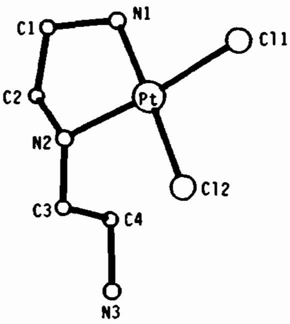

Fig. 1. Numbering scheme of the atoms in the cation.

TABLE II. Bond Lengths (Å) and Bond Angles (°) Within the Cation (e.s.d.s in parentheses)

Pt–Cl1	2.306(4)	C1–C2	1.52(2)
Pt–Cl2	2.303(5)	C2–N2	1.54(2)
Pt–N1	2.045(14)	N2–C3	1.49(2)
Pt–N2	2.069(10)	C3–C4	1.54(2)
N1–C1	1.48(2)	C4–N3	1.54(2)
N1–Pt–N2	84.1(5)	N1–C1–C2	105.9(12)
Cl1–Pt–Cl2	91.2(2)	C1–C2–N2	107.5(11)
N1–Pt–Cl1	91.4(3)	Pt–N2–C2	106.8(9)
N2–Pt–Cl2	93.5(4)	Pt–N2–C3	119.4(8)
N1–Pt–Cl2	176.9(3)	N2–C3–C4	109.5(13)
N2–Pt–Cl1	173.8(3)	C3–C4–N3	107.0(13)
Pt–N1–C1	109.3(10)		

of four different cations at distances ranging from 3.15(2) to 3.23(1) Å.

The platinum atom is coordinated to two chloride ions and the two unprotonated nitrogen atoms of the dienH$^+$ ligand. The coordination polyhedron is planar as expected for a d^8 Pt(II) ion (dsp^2 hybridization). The Pt–Cl and Pt–N bond distances are similar to those reported for *cis*-[Pt(en)Cl$_2$], *cis*-[Pt(bpy)Cl$_2$] and *cis*-[Pt(NH$_3$)$_2$Cl$_2$] [7–9]. The N–C and C–C bond lengths in the dienH$^+$ ligand are normal.

Supplementary Material

The thermal parameters and a listing of the observed and calculated structure factors are available from the authors on request.

Acknowledgements

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the South African Council for Scientific and Industrial Research.

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