Inorganica Chimica Acta, 156 (1989) 29–30

Concerning Ring-opened Diethylenetriamine Complexes of Pt(II). The crystal structure of $[Pt(dienH)Cl_2]_2[PtCl_4]\cdot H_2O$

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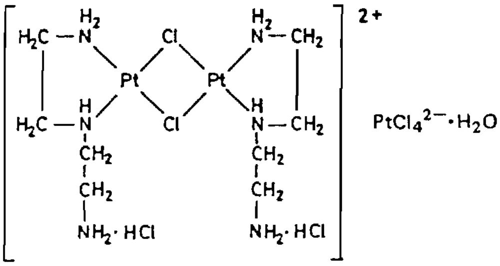
(Received August 25, 1988)

We recently reported evidence for the characterization of a ring-opened diethylenetriamine complex of Pt(II), *viz.* $Pt(dien\cdot HCl)Cl_2$ [1, 2]. Although we have reported indirect evidence for the isolation of a closely related Pd(II) complex before [3], this species was stable enough in acidic aqueous solution to grow crystals for structural analysis. In our first report [1] we referred to a paper by Watt and Cude [4] in which they reported the isolation of a species with formula $Pt_3C_8H_{30}ON_6Cl_8$ and suggested the following structure:



We were also able to isolate a similar species as orange–red crystals [1] but, based on our elemental analysis, preferred a slightly different composition, *viz.* $[(dien\cdot HCl)Pt(\mu\text{-}Cl)_2Pt(dien\cdot HCl)]PtCl_4\cdot HCl\cdot 3H_2O$. We have in the mean time succeeded in growing crystals suitable for structure analysis and, surprisingly, the correct structure is not a chloro-bridged ring-opened species, but merely an ionic salt with formula $[Pt(dienH)Cl_2]_2[PtCl_4]\cdot H_2O$.

Experimental

The complex was prepared and isolated as described before. The crystals exhibited all the chemical and spectroscopic properties reported before [1].

The orange–red compound crystallizes in the monoclinic space group $C2/c$ with $a = 10.664(1)$, $b = 21.863(2)$, $c = 10.319(2)$ Å; $\beta = 94.93(1)°$; $Z = 4$. 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 $0.09 \times 0.14 \times 0.16$ mm was used for the data collection. A total of 3533 reflections were measured, of which 2896 were considered as observed ($I > 3\sigma(I)$). The data were corrected for Lorentz, polarization and absorption effects.

The coordinates of the platinum atoms were determined from a three-dimensional Patterson function. The positional parameters of all the non-hydrogen atoms were deduced from a subsequent Fourier map. A full matrix least-squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms resulted in an R value of 0.041. The final positional parameters with their estimated standard deviations are listed in Table 1. The anisotropic thermal parameters and a listing of the observed and calculated structure factors are available from the authors.

TABLE 1. Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) (e.s.d.s in parentheses)

Atom	x	y	Z	U_{eq} [a]
Pt(1)	0	5000	5000	22.2
Pt(2)	1195.5(3)	1688.6(2)	3826.2(4)	18.1
Cl(21)	−4(3)	923(1)	4625(3)	30.7
Cl(22)	117(3)	2403(1)	4937(3)	25.3
Cl(11)	−6(3)	6008(1)	5616(3)	34.3
Cl(12)	2150(3)	5041(2)	4896(3)	34.3
N(21)	2161(10)	1072(4)	2854(10)	29.8
N(22)	2409(8)	2306(4)	3099(8)	17.7
N(23)	2637(11)	4014(5)	2554(13)	38.7
C(21)	3322(11)	1366(6)	2365(12)	29.0
C(22)	2936(11)	2002(5)	1950(12)	28.9
C(23)	1939(11)	2937(5)	2811(13)	29.6
C(24)	3023(11)	3360(6)	2430(13)	32.8
O(1)	0	254(6)	7500	39.5

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j[U_{ij}(a^*_i a^*_j)(\bar{a}_i\cdot\bar{a}_j)]$.

Results and Discussion

The bond lengths and angles are given in Table 2. The structure consists of discrete $[Pt(dienH)Cl_2]^+$ cations (see numbering scheme in Fig. 1), $PtCl_4^{2-}$ anions and water molecules. The platinum atom of the $PtCl_4^{2-}$ ion (Pt(1)) is situated on a center of symmetry, while the oxygen atom of the water molecule is on a two-fold axis. The $PtCl_4^{2-}$ ion is

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TABLE 2. Bond Lengths (Å) and Angles (°) within the Cation and Anion (e.s.d.s in parentheses)

Pt(1)–Cl(11)	2.293(3)	N(21)–C(21)	1.519(16)
Pt(1)–Cl(12)	2.306(3)	C(21)–C(22)	1.503(16)
Pt(2)–Cl(21)	2.302(3)	C(22)–N(22)	1.509(15)
Pt(2)–Cl(22)	2.303(3)	N(22)–C(23)	1.489(14)
Pt(2)–N(21)	2.015(10)	C(23)–C(24)	1.559(17)
Pt(2)–N(22)	2.055(8)	C(24)–N(23)	1.495(17)
N(21)–Pt(2)–N(22)	83.8(4)		
Cl(21)–Pt(2)–Cl(22)	89.9(1)		
N(22)–Pt(2)–Cl(21)	174.1(2)		
N(21)–Pt(2)–Cl(22)	179.2(3)		
N(21)–C(21)–C(22)	105.9(9)		
C(21)–C(22)–N(22)	107.1(9)		
C(22)–N(22)–C(23)	113.1(9)		
N(22)–C(23)–C(24)	110.9(9)		
C(23)–C(24)–N(23)	109.3(10)		
Cl(11)–Pt(1)–Cl(12)	90.1(1)		
Cl(11)–Pt(1)–Cl(11)[a]	89.9(1)		
Cl(11)–Pt(1)–Cl(12)[a]	180.0(1)		

[a] Related through *T*.

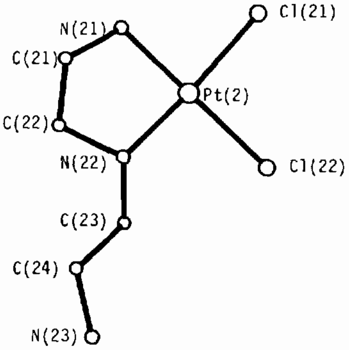

Fig. 1. Numbering scheme of the atoms in the cation.

planar, as required by the symmetry center. The Pt–Cl distances are the same as in the [Pt(dienH)-Cl_2]$^+$ cation, see Table 2.

The platinum atom of the [Pt(dienH)Cl_2]$^+$ cation (Pt(2)) is coordinated to two unprotonated nitrogen atoms of the dienH$^+$ ligand and two chloride ions. Calculation of the best plane through the atoms of the coordination polyhedron showed it to be planar within experimental error, as can be expected for a dsp^2 square-planar hybridization of metal orbitals. The Pt–Cl and Pt–N bond distances are (within experimental error) the same as reported for Pt(dien·HCl)Cl_2 [2], *cis*-[Pt(en)Cl_2] [5], *cis*-[Pt(bpy)Cl_2] [6] and *cis*-[Pt(NH_3)$_2Cl_2$] [7]. The N–C and C–C bond lengths in the dienH$^+$ ligand are normal.

The uncoordinated (protonated) nitrogen atom of the dienH$^+$ ligand has four chloride atoms of two different [$PtCl_4$]$^{2-}$ ions at distances ranging from 3.31(1) to 3.51(1) Å as nearest neighbors. The oxygen atom of the water molecule is weakly hydrogen bonded (O–N = 2.99(1) Å) to the protonated nitrogen atoms of two different [Pt(dienH)-Cl_2]$^+$ ions.

It follows from the structural analysis that the orange–red crystals exhibit the same ring-opened structure as reported for Pt(dien·HCl)Cl_2 [2], which was isolated as light yellow crystals. The misleading red color is therefore not due to the formation of a chloro-bridged species but due to the presence of the $PtCl_4^{2-}$ ion. We assume that Watt and Cude isolated an identical species [4].

Supplementary Material

Thermal parameters are available from the authors on request.

Acknowledgements

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

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