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A Chelate Ring Structure of a Platinum(II) Diborate

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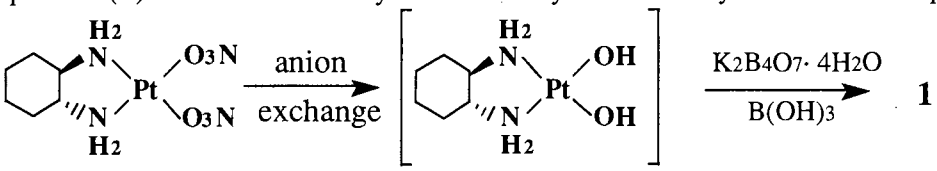
A 1R,2R-diaminocyclohexaneplatinum(II) complex of $B_2O_5H_2^{2-}$, $(C_6H_{14}N_2)Pt(B_2O_5H_2)\cdot 2H_2O$, is synthesized by reacting $(C_6H_{14}N_2)Pt(OH)_2$ with boric acid in the presence of dipotassium tetraborate tetrahydrate in aqueous solution. X-ray structural analysis revealed that the $B_2O_5H_2^{2-}$ anion and the platinum(II) cation form a six-membered chelate.

Considerable effort has been exerted to the crystal structure determination of inorganic borates.1) However, the bad crystal habits hamper the establishment of their stereochemistry except for alkali and alkaline-earth metals. In the course of our work on the exploitation of antitumor platinum agents, a stable crystalline borate complex of platinum(II) has been incidentally obtained. Its synthesis and crystal structure is reported here.



Scheme 1. Synthetic Procedure to a Platinum(II) Borate.

The synthetic procedure is shown in Scheme 1. A 8.6 g of portion of dinitrato[(1R,2R)-1,2-diaminocyclohexane]platinum(II) was dissolved in 200 cm^3 of water with heating. The solution was passed through a column packed with the anion exchange resin(Diaion SA10AOH, 300cm^3) and a further amount of water was passed through the column.[2] To the combined eluate(ca. 500 cm^3), 13.0 g of dipotassium tetraborate tetrahydrate and 0.45 g of boric acid were successively dissolved. After stirring 5 minutes, the solution was evaporated to ca.80 cm^3. By filtration, white powder of $(C_6H_{14}N_2)Pt(B_2O_5H_2)\cdot 2H_2O$, **1**, was obtained(7.3 g, 81% yield). Found: C, 15.96; H, 4.34; N, 6.20. Calcd for $B_2C_6H_{20}N_2O_7Pt$: C, 16.05; H, 4.49; N, 6.24. The borate **1** has an unexpected stability; several recrystallization from hot water gave the identical product but after long exposure to sunlight, **1** turned to light yellow.

A crystal suitable for X-ray analysis was obtained by recrystallization from water. Crystal data of **1** are listed in Table 1 .[3] The molecular structure of **1** is shown in Fig.1. Several things are noticeable on the structure of **1**. First, a diborate group forms six-membered chelate with a platinum atom. In a formal sense, a diborate dianion, $B_2O_5H_2^{2-}$, serves as a chelating reagent to a platinum(II) dication, giving a relatively stable borate complex. This finding opens up the possibilities that other heavy metal(II) ion might make similar chelate complexes. Second, intermolcular interaction(presumably hydrogen-bonding) in a crystal is largely contributed by diborate

moieties. The contribution of amine part is not strong in sharp contrast with those of classical platinum(II) ammine complexes.

Table 1. Crystal Data

Empirical Formula	$PtO_7N_2C_6B_2H_{20}$	Space Group	$P2_12_12_1$
Formula Weight	448.94	Z value	4
Crystal Dimensions	0.20x0.18x0.40 (mm)	Dcalc.	2.274 g/cm^3
Crystal System	orthorhombic	Dobs.	2.29 g/cm^3
Lattice Parameters:	a = 8.240(3) Å	F_{000}	856
	b = 21.988(5)	μ(MoKα)	108.35cm^{-1}
	c = 7.230(3)	No.Observation	1971(I>3.00σ(I))
	V = 1311.2(7) Å^3	Residuals: R; Rw	0.034; 0.046

Distances within a diborate group are not unusual(B-O=1.3~1.4Å).The distances between platinum and donor atoms also have ordinary values, i.e., Pt-O≈2.0Å and Pt-N≈2.0 Å.

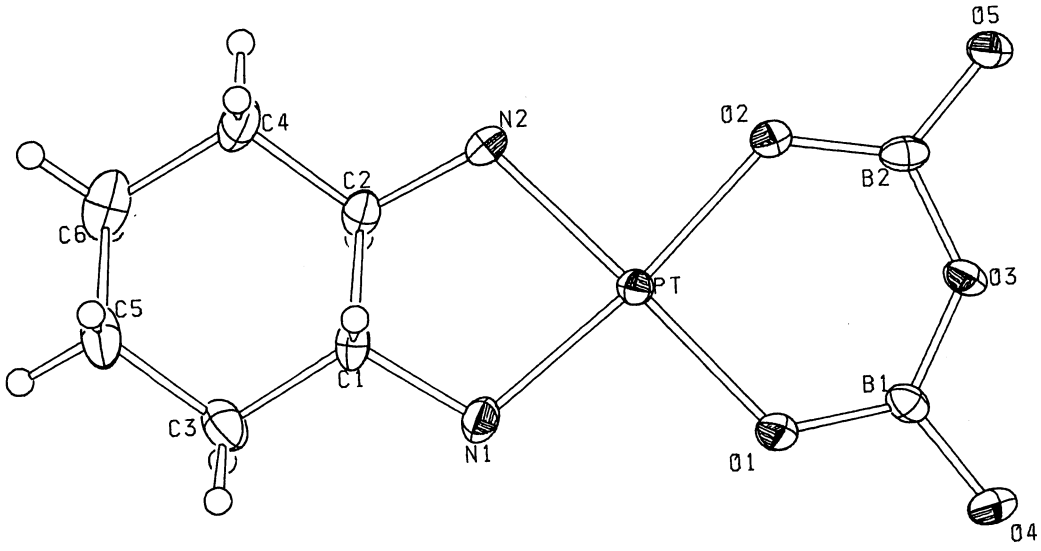


Fig.1. Molecular Structure of ($C_6H_{14}N_2$)Pt($B_2O_5H_2$).

Our effort to make analogous platinum(II) borates, by use of other amine complexes such as dinitrato(1,2-diaminoethane)platinum(II) or cis-dinitratodiammineplatinum(II), have led to the successful isolation of powder samples. The elemental analysis agrees well to the composition $(C_2H_8N_2)Pt(B_2O_5H_2)\cdot 2H_2O$ or $(NH_3)_2Pt(B_2O_5H_2)\cdot 4H_2O$ respectively. However, their bad crystal habits again prevented us from determining the authentic molecular structures.

References

1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed., John Wiley & Sons, New York(1988), p. 170 .
2) T. Totani, K. Aono, M. Komura, and Y. Adachi, Chem. Lett., **1986**, 429.
3) Details of the X-ray structure analysis are reported in the following:H. Ichida and T. Ken Miyamoto, submitted to Acta Crystallogr., Sect. C.

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