Synthesis and Structure of Bis(μ-2-mercaptopyridinato)bis(ethylenediamine)diplatinum(II) Chloride

ISAMU KINOSHITA, YUKO YASUBA,
KEIJI MATSUMOTO and SHUN'ICHIRO OOI

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

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Platinum pyrimidine blues have been attracting much interest as excellent antitumor drugs as well as, from the viewpoint of coordination chemistry, congeners of Platinbrau. The synthesis and complete characterization of the *cis*-diammineplatinum α-pyridone blue by Lippart and coworkers [1] prompted the investigation of the platinum pyrimidine blues and many polynuclear platinum complexes with bridging pyrimidine bases have been prepared. Some of the complexes have been characterized by X-ray analysis [2–9]. However, the reaction of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ with the pyrimidine bases, usually used for the preparation of these complexes, is not always selective for the formation of the polynuclear species.

The Pt(IV) and Pd(II) complexes of 6-mercaptopurine are known to have antitumor activity [10]. We have been attempting the preparation of the Pt(II) complex of 2-mercaptopyridine (mpyH) which has the same kind of donor atom as 6-mercaptopurine and a similar donor atom disposition to α-pyridone, in order to investigate the interaction mode between Pt(II) and the ligand. This communication reports the synthesis and structure of $[(en)Pt(mpy)_2Pt(en)]Cl_2 \cdot 3H_2O$ obtained in reasonable yield (en, ethylenediamine).

The compound was prepared in the following way. $PtCl_2(en)$ was allowed to react with an equimolar amount of the mpyH in water at 35 °C. During the reaction the pH of the solution was kept at 9 by the addition of 0.1 *M* KOH solution. After an equimolar amount of KOH was added to the mpyH, the solution was stirred for 2.5 hr at 35 °C. The pH of the solution was 7 at this point. Rotary evaporation of the solution gave a yellow residue which was found to be composed of the methanol soluble and insoluble parts. The insoluble residue was recrystallized from water. The lemon yellow crystals were analysed to be $[Pt(mpy)(en)]Cl \cdot 1.5H_2O$. Yield: 66%. The characterization of the methanol soluble residue is under way.

The 100 MHz ^1H NMR spectrum of the $[Pt(mpy)(en)]^+$ in D_2O shows an asymmetrical multiplet, assignable to methylene protons, at the 2–4 ppm region from DSS (Fig. 1). The asymmetrical pattern

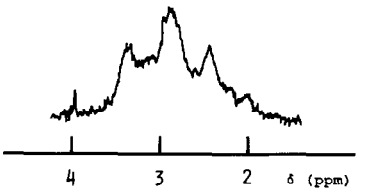

Fig. 1. The methylene proton resonance in the 100 MHz NMR spectrum.

suggests that the complex is not mononuclear $[Pt(mpy)(en)]^+$ but is a dinuclear complex like $[(NH_3)_2Pt(\alpha\text{-pyridonate})_2Pt(NH_3)_2]^{2+}$ [2]: the methylene protons in the monomer should show a symmetrical A_2B_2 spectrum at room temperature because of the rapid $\lambda \leftrightarrow \delta$ conformational interconversion of the en chelate ring, whereas those in the head-tail and head-head dimers should exhibit asymmetrical ABCD and two sets of AA'BB' spectra* respectively, and the AA'BB' patterns may overlap to give an asymmetrical multiplet. The structure was confirmed by X-ray analysis.

Crystal Data: Triclinic, $a = 12.992(2)$, $b = 11.886(2)$, $c = 8.899(2)$ Å, $\alpha = 94.45(2)°$, $\beta = 75.29(2)°$, $\gamma = 112.77(2)°$, space group $P\bar{1}$, $Z = 2$ (in dimer), $\mu(MoK_\alpha) = 124.1$ cm^{-1}. Intensity data were measured on an automated diffractometer by use of graphite-monochromated MoK_α radiation and corrected for absorption. Of 4797 unique reflections collected in the $2\theta \leqslant 52°$ range, 3330 with $F_o^2 > 3\sigma(F_o^2)$ were used for the structure analysis. The structure was solved by the Patterson-Fourier method and refined by least-squares to $R = 0.035$.

Figure 2 shows the structure of $[(en)Pt(mpy)_2Pt(en)]^{2+}$ which resembles that of the head-head isomer of the α-pyridonate complex [2]. The reaction described above thus affords selectively the head-head isomer.

Each Pt atom has a square-planar coordination. The Pt(1) and Pt(2) deviate slightly from respective coordination planes in such a way that two Pt atoms approach each other. This indicates the presence of a weak interaction between the two Pt's. The deviation of Pt(1) from the [2S, 2N] plane is 0.103(3) Å and that of Pt(2) from the [4N] plane is 0.085(5) Å. The Pt···Pt distance is 3.083(1) Å. The [4N] plane is slant against the [2S, 2N] plane, the interplanar angle being 31.0(2)°. The S(11)–Pt(1)–Pt(2)–N(11) and S(21)–Pt(1)–Pt(2)–N(21) torsion angles are 36.4(3)° and 28.7(3)° respectively. The Pt···Pt distance and

*Such spectral patterns for the dimers result from the methylene protons under rapid thermal molecular motion (oscillation of two coordination squares about the Pt···Pt axis and conformational interconversion of the en ring).

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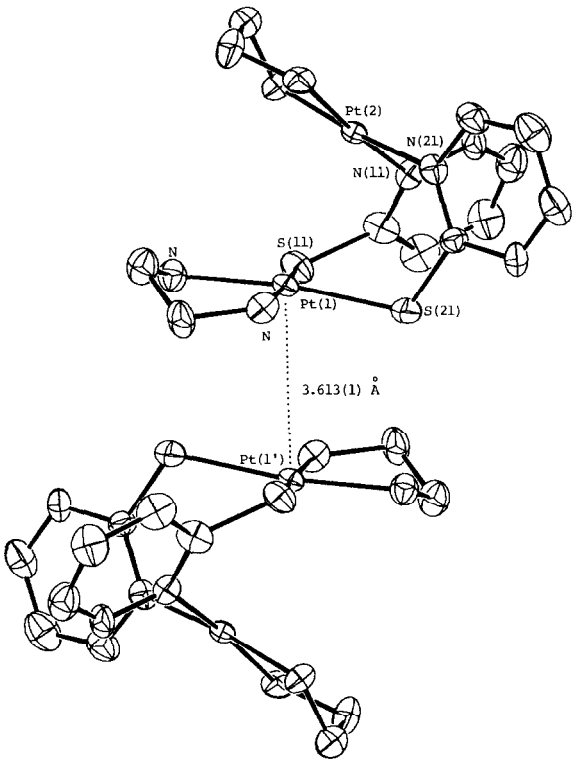

Fig. 2. The structure of $[(en)Pt(mpy)_2Pt(en)]^{2+}$ and that of the dimer pair.

torsion angles are larger than those in the α-pyridonate [2], 1-methyluracilate [4] and 1-methylthyminate [5–7] dimers. The longer N···S bite (2.72 Å) in the mpy than the N···O in the pyrimidine bases may be responsible for the increase in these molecular parameters. Some important bond lengths and angles are as follows: Pt–S = 2.300 (4) Å, Pt–N-(pyridine) = 2.05(1) Å, Pt–N(en) = 2.08(1) Å (*trans* to S), 2.05(1) Å (*trans* to pyridine N), N(en)–Pt–N(en) = 83.4(5)°, S–Pt–S = 94.8(1)°.

In the crystal structure two dimers are linked together as shown in Fig. 2. The crystallographic center of symmetry lies on the mid point of Pt(1)··· Pt(1′). The dimer pair is held by N–H···S interaction (N···S = 3.34, 3.51(1) Å).

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