

Amino Acid Complexes of Platinum(IV). VI. Ethylenediamine-tetraacetate (EDTA) Complexes*

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Three isomers of $Pt(EDTAH_2)Cl_2$, with the ligand tetradentate, have been isolated. The isomer with chloro ligands trans is the initial product of chlorine oxidation of $Pt(EDTAH_2)$, but may be converted readily to thermodynamically more stable isomers with chloro ligands cis. These latter two isomers may also be isolated from direct reaction of K_2PtCl_6 and $Na_2(EDTAH_2)$, and from chlorine oxidation of $Pt(EDTAH_4)Cl_2$. $Pt(EDTAH_4)Cl_4$ (bidentate ligand) and $Pt(EDTAH_3)Cl_3$ (tridentate ligand) are intermediates in these reactions. The trichloro complex may be isolated. Conversion of $Pt(EDTAH_3)Cl_3$ to the isomers of $Pt(EDTAH_2)Cl_2$ provides an interesting example of the operation of the trans effect.

Introduction

Ethylenediamine-tetraacetate complexes have been characterized for a very wide range of metal ions, including platinum(II), for which the complexes (1) and (2) have been well characterized [1].



Surprisingly little is known of platinum(IV) complexes with EDTA. It has been shown that $PtCl_6^{2-}$ forms a 1:1 complex with EDTA in dilute aqueous solution, postulated to be $Pt(EDTAH)Cl_4^{3-}$, and that this reaction may be used to estimate Pt(IV), but no solid complex was isolated [2]. It has been reported [3] that 'Pt(OH)₄' dissolves in a 0.05 M EDTA

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†The abbreviation EDTAH₄ refers to the fully protonated free acid.

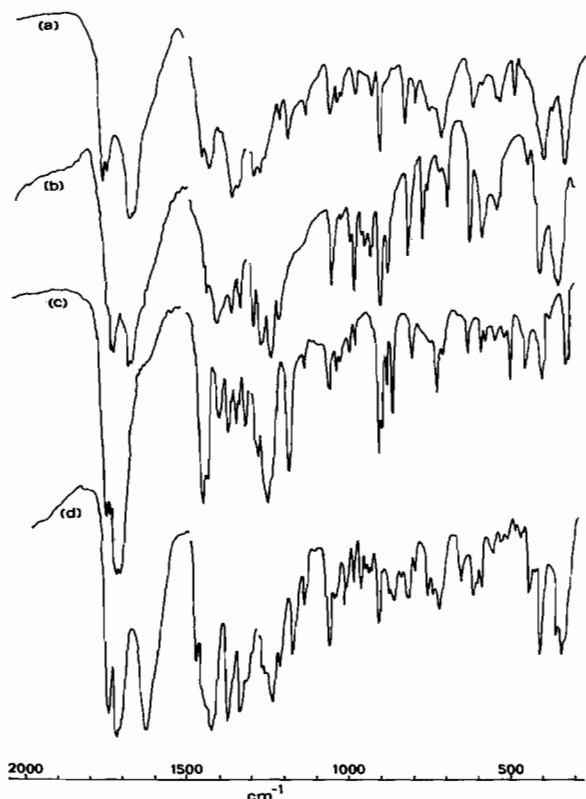
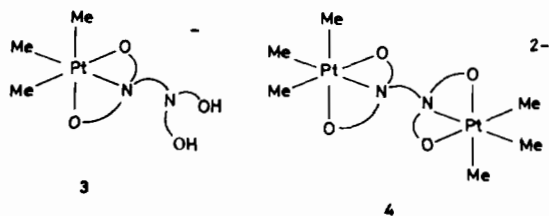


Fig. 1. Infra-red spectra (2000–250 cm^{-1}). (a) $Pt(EDTAH_2)Cl_2 \cdot H_2O$ (5) (Isomer A). (b) $Pt(EDTAH_2)Cl_2 \cdot 2H_2O$ (6) (Isomer B). (c) $Pt(EDTAH_2)Cl_2 \cdot H_2O$ (7) (Isomer C). (d) $Pt(EDTAH_3)Cl_3$ (12). The region 1500–1350 cm^{-1} is from spectra run as hexachlorobutadiene mulls. The remainder is from spectra run as nujol mulls.

solution at pH 2. Reactions of EDTA with Pt(II) and Pt(IV) to give $Pt(EDTAH_4)X_2$ ($X = Cl, Br, OH$), $Pt(EDTAH_2)Br_2$, and $Pt(EDTAH_2)Br(OH)$ have been reported [4, 5], but these papers are not readily accessible. Apart from these the only platinum(IV) EDTA complexes characterized have been the trimethylplatinum(IV) complexes (3) and (4) [6].



In this paper, we report the preparation of platinum(IV) EDTA complexes by oxidation of the platinum(II) complexes (1) and (2), and by direct reaction of K_2PtCl_6 and $Na_2(EDTAH_2)$. There are some parallels between our results and those reported for platinum complexes of ethylenediaminediacetic acid (EDDAH₂) by Liu [7].

Results and Discussion

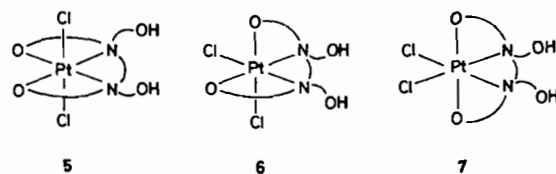
Chlorine Oxidation of $Pt(EDTAH_2)$ (2)

When chlorine was passed through a suspension of $Pt(EDTAH_2) \cdot 3H_2O$ (2) in a small volume of water, the solid dissolved and the solution turned yellow. Shortly after chlorine flow was discontinued, a pale yellow solid began to precipitate, which is insoluble in methanol, ethanol, and acetone, sparingly soluble in water, and analyses for $Pt(EDTAH_2)Cl_2 \cdot H_2O$. Its IR spectrum (Fig. 1a) shows carboxyl stretching frequencies at 1775, 1764, 1691 and 1678 cm^{-1} . From IR results on a large number of EDTA complexes, it has been concluded that free unionized $-COOH$ groups usually give carboxyl bands above 1700 cm^{-1} , free deprotonated carboxylate groups usually give bands near 1600 cm^{-1} , and carboxylate coordinated to metals bands between 1600 and 1700 cm^{-1} [8–11]. The spectrum of the product is therefore consistent with the presence of both protonated and coordinated carboxyl groups, as would be expected for a complex with the ligand tetradentate. The spectrum also shows bands in the region expected for $\nu(Pt-Cl)$, *viz.*, 357 and 350 cm^{-1} . This complex is labelled as isomer A of $Pt(EDTAH_2)Cl_2$.

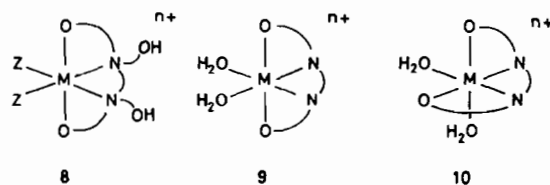
If (2) was suspended in a larger volume of water, and the chlorination reaction carried out as before, a precipitate did not begin to form until about 30 minutes after chlorine addition. This pale yellow solid is insoluble in cold water and common organic solvents. It analyses for $Pt(EDTAH_2)Cl_2 \cdot 2H_2O$, and gives a different IR spectrum from isomer A (Fig. 1b), with carboxyl stretching bands at 1758, 1742, 1692 and 1685 cm^{-1} , and a band assigned to $\nu(Pt-Cl)$ at 342 cm^{-1} , with a shoulder at 351 cm^{-1} . This product is labelled isomer B of $Pt(EDTAH_2)Cl_2$. It was found that isomer B could also be prepared by suspending isomer A in water, heating until it dissolved, then allowing the solution to stand until isomer B precipitated.

If an aqueous suspension of isomer A was heated on a steam bath after the compound dissolved, a pale yellow solid precipitated from the hot solution after 15 minutes. This precipitate is insoluble in common organic solvents, and in hot water. It analyses for $Pt(EDTAH_2)Cl_2 \cdot H_2O$, and gives an IR spectrum different from those for isomers A and B (Fig. 1c). Carboxyl stretching frequencies are observed at 1753, 1741, 1725, and 1716 cm^{-1} and $\nu(Pt-Cl)$ bands at 338 and 326 (shoulder) cm^{-1} . Although the two lower frequency carboxyl bands are above the usual empirical frequency range for coordinated carboxylate [8–11] the compound is formulated as containing tetradentate $EDTAH_2^{2-}$, and is labelled isomer C of $Pt(EDTAH_2)Cl_2$. Isomer C may also be obtained by heating isomer B in water at 80 °C.

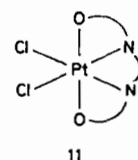
There are three possible isomers of $Pt(EDTAH_2)_2Cl_2$ (5), (6) and (7).



Isomer (5) would be expected to be the least stable thermodynamically of the three, and isomer (7) the most stable, with (6) being intermediate, because of the angle strain involved in coordination of the acetate chains equatorially. Coordination of type (8) has always been found for complexes which have been characterized, of tetradentate $EDTAH_2$ with octahedral metal ions. (*e.g.* $NH_4[VO_2(EDTAH_2)] \cdot 3H_2O$ [12], $H[RhX_2(EDTAH_2)] \cdot 2H_2O$ ($X = Cl, Br$) [13], $[Ru(EDTAH_2)L_2] \cdot 2H_2O$ ($L = MeCN, py, 1,10\text{-phen, etc.}$) [14]).

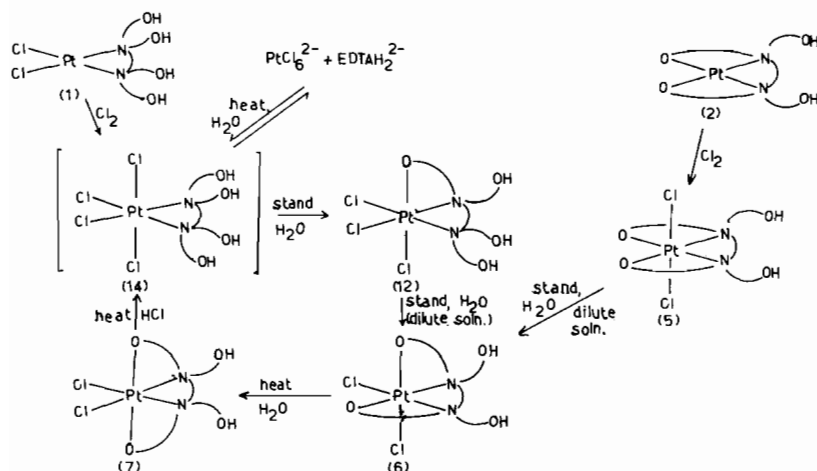


For the related ligand ethylenediaminediacetate (EDDA) the only isomer reported for $Ni(EDDA)(H_2O)_2$ has structure (9) [15]. For $Cr(EDDA)(H_2O)_2^+$ [16] and $Co(DDA)(H_2O)_2^+$ [17] only isomers (9) and (10) have been isolated, and for $M = Co$, (10) isomerizes to (9) on standing in water. For $PtCl_2(EDDA)$, the only isomer obtained is (11) [7] (although other, less stable isomers might possibly be obtainable using different conditions or reactions).



Isomer A is assigned as (5), since oxidative addition of chlorine to platinum(II) complexes is *trans* across the coordination plane [7, 18–20]. Isomer A is also the least stable thermodynamically, since it isomerizes on heating to isomers B and C, consistent with the assignment of structure (5).

Isomer C, the end product if either A or B is heated, is the most stable thermodynamically, and so is assigned as (7). This leaves isomer B, intermediate in stability, assigned as (6).



Scheme 1. Preparation and interconversion reactions of platinum(IV)–EDTA complexes.

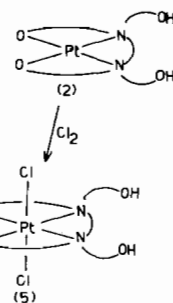
The reaction scheme for chlorine oxidation of $\text{Pt}(\text{EDTAH}_2)$ (2) is summarized in Scheme 1. Isomerization of (5) to (6) to (7) involves two successive migrations of carboxyl O from the equatorial plane to 'axial' sites.

Chlorine Oxidation of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ (1)

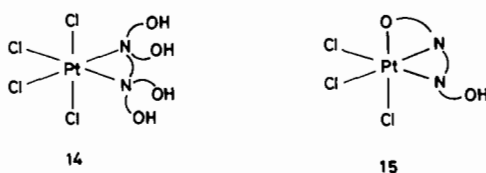
When chlorine was passed through an aqueous suspension of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (1), the compound dissolved and the solution turned dark yellow. After five minutes, chlorine flow was stopped, and after a further 15 minutes a pale yellow solid precipitated, identical in all respects to $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6) obtained from chlorine oxidation of $\text{Pt}(\text{EDTAH}_2) \cdot 3\text{H}_2\text{O}$.

When this reaction was repeated with a smaller volume of water, a yellow precipitate formed in only five minutes after chlorine addition was stopped. This solid is insoluble in common solvents, and in water, and analyses for $\text{Pt}(\text{EDTAH}_3)\text{Cl}_3$. Its IR spectrum (Fig. 1d) is more complex than that for any of the isomers of $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$. Carboxyl peaks occur at 1759, 1730, 1721 and 1635 cm^{-1} , indicating the presence of both protonated and metal-bound carboxyl groups. Strong bands at 359 and 341 cm^{-1} and possibly a shoulder at 353 cm^{-1} may be assign-

ed to $\nu(\text{Pt}-\text{Cl})$ modes. These data are consistent with tridentate coordination of EDTAH_3^- , previously unknown in a non-organometallic octahedral complex. The two isomers possible are (12) and (13).



Isomer (12) would be expected to be more stable thermodynamically than (13), because of angle strain involved in coordinating the acetate chain equatorially, as discussed above. The initial product of the oxidation of (1) would be expected to be $\text{Pt}(\text{EDTAH}_4)\text{Cl}_4$ (14), which can form isomer (12) by ring closure axially, and (13) by ring closure equatorially. Because the *trans* effect of N-donors is less than that of chloride [21], the axial chloride in (14) (*trans* to Cl) will be more labile than equatorial chloride (*trans* to N). Hence ring closure to an axial site should be faster, and (12) would be expected to be the kinetically favoured product, as well as the thermodynamically preferred product. The product with tridentate ligand is therefore assigned as (12). Liu [7] reported that chlorine oxidation of $\text{Pt}(\text{EDDAH}_2)\text{Cl}_2$ yielded $\text{Pt}(\text{EDDAH})\text{Cl}_3$ (15).



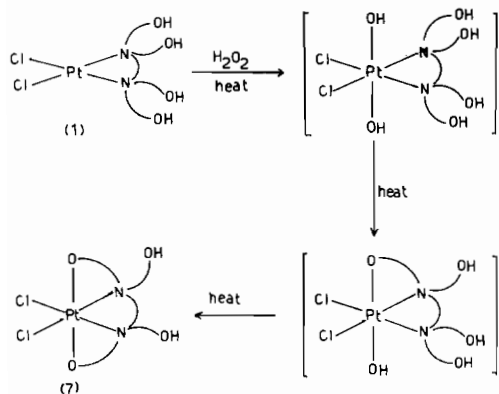
Further reaction of (12) to $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ could occur by ring closure equatorially to give (6)

or axially to give (7). The formation of (6) rather than the thermodynamically more stable (7) is an illustration of the operation of the trans effect. The equatorial chloride ligands in (12) are *trans* to N, which has a higher trans effect than O, *trans* to the axial Cl atom. Ring closure therefore occurs equatorially to give (6) as the kinetic product. Heating an aqueous suspension of either $\text{Pt}(\text{EDTAH}_3)\text{Cl}_3$ (12) or $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ (6) does, of course, ultimately produce the thermodynamically preferred isomer of $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$, (7).

These reactions are summarized in Scheme 1.

Peroxide Oxidation of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ (1)

When a suspension of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (1) in water was heated with hydrogen peroxide the solid dissolved and the solution turned yellow. On prolonged heating the solution lightened in colour, and $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ (isomer (7)) precipitated. In peroxide oxidations, two OH groups usually add *trans* across the Pt(II) coordination plane [19]. The proposed reaction sequence is therefore as shown in Scheme 2.



Scheme 2. Peroxide addition to $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ (1).

Attempts to oxidize $\text{Pt}(\text{EDTAH}_2) \cdot 3\text{H}_2\text{O}$ (2) with hydrogen peroxide yielded a mixture of water-soluble compounds, none of which has been identified.

Reaction of PtCl_6^{2-} with EDTAH_2^-

When a solution of $\text{Na}_2(\text{EDTAH}_2)$ was added to an aqueous suspension of an equimolar quantity of K_2PtCl_6 , and the mixture was heated on a steam bath for 1.5 hours, a pale yellow precipitate of $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ (isomer (7)) was formed. The same product was obtained from reaction of Na_2PtCl_6 with $\text{Na}_2(\text{EDTAH}_2)$ and by reaction of K_2PtCl_6 with $\text{K}_2(\text{EDTAH}_2)$.

If the reaction between K_2PtCl_6 and $\text{Na}_2(\text{EDTAH}_2)$ was repeated, but with the reaction mixture heated to only 40 °C, a precipitate formed after

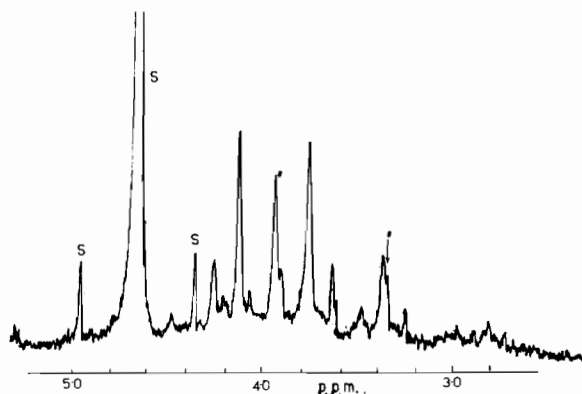


Fig. 2. ^1H n.m.r. spectrum in 1 M $\text{DCl}/\text{D}_2\text{O}$ solution of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_4$ (14). # EDTAH_4 impurity. S HDO peak and associated spinning side bands.

30 minutes. This product was $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (isomer (6)), contaminated with EDTAH_4 . If heating of the reaction mixture at 40 °C was prolonged, the solid obtained was a mixture of (6) and (7), still contaminated with EDTAH_4 . Analytically pure samples of (6) are therefore better prepared by oxidative addition of chlorine to $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ (1). Prolonged heating of this product did, of course, convert it to isomer (7).

The filtrate after precipitation and filtration of (7) was evaporated to dryness in a vacuum desiccator and extracted with acetone. The acetone was removed from the solution under reduced pressure to give an orange solid, which is soluble in methanol, ethanol, acetone, and water. When a solution of this compound in any solvent was allowed to stand, a yellow precipitate of $\text{Pt}(\text{EDTAH}_3)\text{Cl}_3$ (12) formed, which was identified by its IR spectrum. If the orange solid was allowed to stand in air, it absorbed moisture, and eventually formed (12). Even in the absence of moisture, the solid slowly tended to decompose, and a pure sample was not obtained. The same product (with EDTAH_4 and PtCl_6^{2-}) could be produced in solution by heating $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ (isomer (6) or (7)) with dilute HCl. This species is assigned as $\text{Pt}(\text{EDTAH}_4)\text{Cl}_4$ (14). Solutions in approx. 1 M DCl solution are sufficiently stable to allow a ^1H n.m.r. spectrum to be run. The spectrum is shown in Fig. 2.

The methylene protons on each acetate arm are non-equivalent, and so give an AB spectrum, superimposed on an ABX spectrum from those molecules containing ^{195}Pt ($I = \frac{1}{2}$, 33.6% abundance); δ_{H_A} 4.19 p.p.m., $^3J_{\text{Pt}-\text{N}-\text{C}-\text{H}_A}$ 7.2 Hz, δ_{H_B} 3.71 p.p.m., $^3J_{\text{Pt}-\text{N}-\text{C}-\text{H}_B}$ 38.1 Hz, $J_{\text{H}_A\text{H}_B}$ 14.0. The $\text{NCH}_2\text{CH}_2\text{N}$ protons give a singlet at δ 3.38 p.p.m. with satellites, $^3J_{\text{Pt}-\text{N}-\text{C}-\text{H}}$ 24.8 Hz. The spectrum is entirely consistent with the postulated structure (14). Peaks due to free EDTAH_4 are also present.

The overall reaction of PtCl_6^{2-} is as shown in Scheme 1. The N-atoms of the ligand coordinate first to give $\text{Pt}(\text{EDTAH}_4)\text{Cl}_4$. Thereafter, the scheme is identical to that for chlorine oxidation of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$, except that, under the experimental conditions, $\text{Pt}(\text{EDTAH}_3)\text{Cl}_3$ (12) is not isolated. This scheme is analogous to that given by Liu [7] for reaction of PtCl_6^{2-} with EDDA^{2-} , except that Liu did not report the isolation of a compound analogous to (6).

None of the reactions provided any evidence for formation of a complex with EDTA quinque- or sexa-dentate. The reluctance of the large Pt(IV) cation to form a complex with EDTA sexadentate will be mainly due to the strain involved with this type of coordination. Also, even with a five-fold excess of ligand there was no evidence for formation of any complex containing two EDTA ligands per Pt atom.

$\text{Pt}(\text{EDTAH}_2)\text{Cl}_2$ (7) does dissolve in dilute alkali solution, but addition of acid does not immediately reprecipitate (7), as might be expected for a simple deprotonation of the free carboxyl groups. It is probable that the Pt-Cl bonds are partially replaced by Pt-OH, as has been shown for solutions of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ (1) in alkaline solution [22].

Experimental

Instrumentation

Infrared spectra were run on a Perkin-Elmer 283-b instrument as nujol and hexachlorobutadiene mulls. 100 MHz ^1H spectra were run on a Jeol PS-100 instrument. C, H, and N analyses were carried out by J. Kent and P. Nobbs of this Department. Platinum was determined by ignition after treatment with conc. sulfuric acid.

Starting Compounds

$\text{Pt}(\text{EDTAH}_4)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (1) and $\text{Pt}(\text{EDTAH}_2) \cdot 3\text{H}_2\text{O}$ (2) were prepared by the methods of Busch and Bailar [1]. $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ is quite soluble in acetone. Erickson *et al.* [22] have reported the ^1H n.m.r. spectrum of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$ in DCl solution, but it is of low quality in this medium. A better ^1H spectrum, and a ^{13}C spectrum were obtained in acetone- d_6 (25.5 MHz ^{13}C spectrum, Jeol FX100 instrument, 10,000 scans. 16K data points, double precision mode). ^1H spectrum, acetate methylene group δ_{H_A} 4.67 p.p.m., $^3J_{\text{Pt-N-C-H}_A}$ 7.6 Hz, δ_{H_B} 4.13 p.p.m., $^3J_{\text{Pt-N-C-H}_B}$ 44.4 Hz, J_{AB} 17.5 Hz. $\text{NCH}_2\text{CH}_2\text{N}$: δ_{H} 3.59 p.p.m., $^3J_{\text{Pt-N-C-H}}$ 27.5 Hz. ^{13}C spectrum, δ_{CH_2} (acetate) 59.60 p.p.m., $^2J_{\text{Pt-N-C}}$ 22.7 Hz, $\delta_{\text{N-CH}_2-\text{CH}_2\text{N}}$ 57.04 p.p.m., $^2J_{\text{Pt-N-C}}$ 9.7 Hz, δ_{CO_2} 171.18 p.p.m., $^3J_{\text{Pt-N-C-C}}$ 38.1 Hz.

Preparation of $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$ (5) (isomer A)

0.1 g $\text{Pt}(\text{EDTAH}_2) \cdot 3\text{H}_2\text{O}$ (2), was suspended in 5 ml water and chlorine was bubbled through the suspension for five minutes. The solid dissolved to give a yellow solution. A pale yellow solid began to precipitate after a further five minutes. The mixture was allowed to stand for 30 minutes. The solid was filtered off, washed with ice cold water, then acetone, and dried under vacuum, to give 0.06 g (56%) $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$ (5). *Anal. Calc.* for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_9\text{Cl}_2\text{Pt}$: C, 20.9; H, 2.8; N, 4.9; Pt, 34.0. *Found:* C, 20.7; H, 2.7; N, 4.9; Pt, 34.0.

Preparation of $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6) (isomer B)

By chlorine oxidation of $\text{Pt}(\text{EDTAH}_2)$

0.1 g $\text{Pt}(\text{EDTAH}_2) \cdot 3\text{H}_2\text{O}$ (2) was suspended in 10 ml water. Chlorine was bubbled through the suspension for five minutes, causing the solid to dissolve. A pale yellow solid began to precipitate after 30 minutes. The mixture was allowed to stand for 2 hours. The solid was filtered off, washed with water, then acetone, and dried under vacuum. Yield was 0.08 g (73%) $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6). *Anal. Calc.* for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_{10}\text{Cl}_2\text{Pt}$: C, 20.3; H, 3.1; N, 4.7; Pt, 32.9. *Found:* C, 20.1; H, 2.7; N, 4.8; Pt, 32.8.

By chlorine oxidation of $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2$

0.1 g $\text{Pt}(\text{EDTAH}_4)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (1) was suspended in 10 ml water, and chlorine was bubbled through the suspension for five minutes. The compound dissolved. After 15 minutes, a pale yellow solid began to precipitate. The mixture was allowed to stand for two hours, then filtered off, washed with water, then acetone, and dried under vacuum. Yield was 0.065 g (72%). *Anal. Found:* C, 20.2; H, 2.8; N, 4.7; Pt, 32.8.

From K_2PtCl_6

0.3 g solid $\text{Na}_2(\text{EDTAH}_2) \cdot 2\text{H}_2\text{O}$ (0.892 mmol) was added to a suspension of 0.4 g K_2PtCl_6 (0.823 mmol) in 15 ml water. The mixture was stirred until $\text{Na}_2(\text{EDTAH}_2)$ dissolved, then heated with stirring to 80 °C on a steam bath. When the K_2PtCl_6 had dissolved, the stirring was stopped, and the solution was heated at 40 °C on a hot plate for 30 minutes, during which a pale yellow precipitate had formed. The precipitate was filtered while the mixture was still warm, washed with 2 ml ice-cold water, then 5 ml acetone, and dried under vacuum, to give 0.360 g product. IR spectra showed the product to be predominantly $\text{Pt}(\text{EDTAH}_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6), but examination under a microscope revealed colourless crystals mixed with the pale yellow solid, and analytical results (given below) were high for C, H, and N, indicating contamination by EDTAH_4 . *Anal. Found:* C, 22.3; H, 3.3; N, 5.2.

*Preparation of Pt(EDTAH₂)Cl₂·H₂O (7) (isomer C)**From Pt(EDTAH₂)Cl₂·2H₂O (6)*

0.1 g Pt(EDTAH₂)Cl₂·2H₂O (6) was suspended in 10 ml water and heated on the steam bath. The compound dissolved. Heating was continued until a pale yellow precipitate began to form. The mixture was then allowed to cool to ambient temperature, the solid was filtered off, washed with water, then acetone, and dried under vacuum. Yield was 0.075 g Pt(EDTAH₂)Cl₂·H₂O (7) (77%). *Anal.* Calc. for C₁₀H₁₆N₂O₈Cl₂Pt: C, 20.9; H, 2.8; N, 4.9; Pt, 34.0. Found: C, 20.7; H, 2.5; N, 5.1; Pt, 34.0.

By peroxide oxidation of Pt(EDTAH₄)Cl₂ (1)

0.1 g Pt(EDTAH₂)Cl₂·5H₂O was suspended in 5 ml water and 5 ml 30% H₂O₂ solution was added. The mixture was heated on a steam bath for 1.5 hours, during which time a solid precipitated. The mixture was allowed to cool, and the solid was filtered off, washed with water, then acetone, and dried under vacuum. 0.05 g (56%) Pt(EDTAH₂)Cl₂·H₂O (7) was obtained. *Anal.* Found: C, 21.0; H, 2.6; N, 5.0; Pt, 33.8.

From K₂PtCl₆

0.3 g Na₂(EDTAH₂)·2H₂O (0.892 mmol) was added to a suspension of 0.4 g K₂PtCl₆ (0.823 mmol) in 15 ml water, and the mixture was stirred until Na₂(EDTAH₂) had dissolved. The solution was then heated with occasional stirring at 80 °C on a steam bath for 1.5 hours. During this time, K₂PtCl₆ dissolved, pH fell from 5 to 1.5, and a pale yellow precipitate formed. The precipitate was filtered off quickly from the hot solution, washed with 2 ml hot water, then 5 ml acetone, and dried under vacuum. 0.204 g (43% yield) Pt(EDTAH₂)Cl₂·H₂O (7) was obtained as fine pale yellow needles. *Anal.* Found: C, 20.6; H, 2.9; N, 5.0; Pt, 34.0.

When the volume of the filtrate was reduced on the steam bath, a further 0.2 g product was obtained, but this was contaminated by EDTAH₄.

Preparation of Pt(EDTAH₃)Cl₃ (12)

0.1 g Pt(EDTAH₄)Cl₂·5H₂O was suspended in 5 ml water, and chlorine was bubbled through the solution for five minutes. The compound dissolved. The solution was allowed to stand for 20 minutes, during which time a yellow solid precipitated. The solid was filtered off, washed with water, then acetone, and air dried. 0.055 g Pt(EDTAH₃)Cl₃ (12) (61% yield) was obtained. *Anal.* Calc. for C₁₀H₁₅N₂O₈Cl₃Pt: C,

20.3; H, 2.6; N, 4.7; Pt, 32.9. Found: C, 20.0; H, 2.8; N, 4.7; Pt, 33.0.

The filtrate was allowed to stand overnight. 0.015 g Pt(EDTAH₂)Cl₂·2H₂O (6) was obtained.

Acknowledgements

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