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# CRYSTAL STRUCTURE AND SOLVOLYSIS OF DINITRATO-2,2'-BIPYRIDINE PLATINUM (II) 

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#### Abstract

The crystal structure of dinitrato-2,2bipyridineplatinum(II) $\left[\mathrm{Pt}(\right.$ bipy $\left.)\left(\mathrm{ONO}_{2}\right)_{2}\right]$, as its solvate with 2-propanone (acetone) and its solvolysis in dimethyl sulphoxide (DMSO) to produce $\left[\mathrm{Pt}(\text { bipy })\left(\mathrm{ONO}_{2}\right)(\mathrm{S}-\mathrm{DMSO})\right]^{+}$ are studied through ${ }^{1} \mathrm{HNMR}$ and conductance.

The solvolysis by DMSO was studied for the complex cis-[Pt(2-methylpyridine) $)_{2} \mathrm{I}_{2}$ ]. Satisfactory model for the behavior of a DMSO ligand coordinated to platinum(II) via sulphur was found. Secondly, the going research on many cis-bis-(2-methylpyridine)platinum(II) and palladium(II) residues indicates atropisomerism in solution, through restricted rotation of the pyridine rings about their $\mathrm{N} \rightarrow \mathrm{Pt}$ bonds in ionic compounds like $\left[(\text { phen })(2-\mathrm{Mepy})_{2} \mathrm{Pt}\right]^{2+}$.


## INTRODUCTION

Compounds of 2,2-bipyridyl (bipy) with platinum(II) have attracted a good deal of attention [Bielli et al., (1974)]. The monomers $\left[\mathrm{Pt}(\right.$ bipy $) \mathrm{X}_{2}$ ] include two compounds, yellow and red dimorphs where $\mathrm{X}=$ $\mathrm{Cl}^{-}$[Morgan \& Burstall (1936)]. The structures of the yellow and the red dimorph are known [Osborn \& Rogers (1974) and Textor \& Oswald (1974)]. The flat complex molecules are packing differently in the crystals.

The compounds with $\mathrm{X}=\mathrm{OH}^{-}$or $\mathrm{NO}_{3}{ }^{-}$were made [Bielli et al., (1974)] as possible hydrolysis products of the dihalo-monomer in differing media. The aqueous system has recently been re-examined. The existence of the dinitrato-compound (A) was confirmed but its stability was questioned, in particular in relation to such hydrolysis. The
occurrence of dimeric cations of compositions $\left[\mathrm{Pt}_{2}(\text { bipy })_{2}(\mu-\mathrm{OH})_{2}\right]^{2+}$ and $\left[\mathrm{Pt}_{2}(\mathrm{bipy})_{2}(\mathrm{OH})_{3}\right]^{+}$have been demonstrated [Castan et al., (1990) and Wimmer et al., (1989)] and formed during the reaction of (A) with base.

We report here the crystal structure of $\left[\mathrm{Pt}(\mathrm{bipy})\left(\mathrm{ONO}_{2}\right)_{2}\right]$ (A), as its solvate with 2-propanone (acetone) and also its solvolysis in dimethyl sulphoxide $\left[\mathrm{Pt}(\right.$ bipy $)\left(\mathrm{ONO}_{2}\right)(S \text {-DMSO) }]^{+}$(B) (equation 1). The complexes are studied through ${ }^{1} \mathrm{H}$ NMR and conductance.

$$
\begin{equation*}
\left[\mathrm{Pt}(\text { bipy })\left(\mathrm{ONO}_{2}\right)_{2}\right]+\mathrm{DMSO} \rightarrow\left[\mathrm{Pt}(\text { bipy })\left(\mathrm{ONO}_{2}\right)(S \text {-DMSO })\right]^{+}+\mathrm{NO}_{3}^{-} \tag{1}
\end{equation*}
$$

(A)
(B)

Similar solvolysis by DMSO had been reported [Ha, et al., (1990)] for cis-[Pt(2-methylpyridine $\left.)_{2} \mathrm{I}_{2}\right]$ (C). We have also studied the system for two reasons. First, it gives a satisfactory model for the behavior of a DMSO ligand coordinated to platinum(II) via sulphur. Secondly, we recently discovered that many cis-bis-(2methylpyridine)platinum(II) and palladium(II) residues give rise to atropisomerism in solution, through restricted rotation of the pyridine rings about their $N \rightarrow P t$ bonds in ionic compounds like [(phen)(2Mepy $\left.)_{2} \mathrm{Pt}\right]^{2+}$. It seemed possible that a similar phenomenon might arise in the ostensibly simple $c i s-\left[\mathrm{Pt}(2-\mathrm{Mepy})_{2} \mathrm{I}_{2}\right]$. This, from models, is actually very crowded sterically and it does isomerize [Ha, et al., (1990)] to a trans-diiodo species, like many other cis-diiodo-complexes. However, we now show that the two sets of proton resonance spectra due to 2 --methy! pyridine in a solution of (C) in DMSO do indeed arise from that molecule bound and free.

## EXPERIMENTAL

1- Preparation of Dinitrato-2,2-bipyridineplatinum(II), [Pt(bipy) $\left(\mathrm{ONO}_{2}\right)_{2} \mathrm{l}(\mathrm{A}):$

A solution of $\left[\mathrm{Pt}(\right.$ bipy $\left.) \mathrm{I}_{2}\right](0.77 \mathrm{~g}, 1.27 \mathrm{mmol})$ in acetone ( 50 ml ) was set to reflux for about 30 minutes in the presence of silver nitrate $(0.47 \mathrm{~g}, 2.8 \mathrm{mmol})$ dissolved in water ( 2 ml ) until the reaction mixture was almost colorless. The precipitated silver iodide was removed by filtration and the filtrate kept cold for few days. The shiny yellow needles (not illustrated) were separated and filtered off, washed with acetone and ether and dried under vacuum over silica gel to give 0.4 g of
$\left[\mathrm{Pt}(\right.$ bipy $\left.)\left(\mathrm{ONO}_{2}\right)_{2}\right] \bullet\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}, 62 \%$ yield. The $\mathrm{C}, \mathrm{H}$, and N analyses for $\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{Pt}$ (after removing the solvating $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$ by gentle warming) have been made. Anal. Calcd. for $\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{Pt}: \mathrm{C}, 25.26 ; \mathrm{H}, 1.68$; $\mathrm{N}=11.78 \%$. Found: C, $25.6 ; \mathrm{H}, 1.7 ; \mathrm{N}, 11.6 \%$.

The structure of the solvated complex $\left[\mathrm{Pt}(\mathrm{bipy})\left(\mathrm{ONO}_{2}\right)_{2}\right]$ • $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$ (A) was determined by X-ray crystallography. The crystallographic data for complex (A) are assembled in Table 1.

Table (1): Crystal Data and Structure Refinement for [Pt(bipy) $\left.\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot 0.5\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$

| Identification code | 93CAR033 |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{12}{ }_{5} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6}{ }_{5} \mathrm{Pt}$ |
| Formula weight | 513.31 |
| Temperature | 293(2) K |
| Wavelength | 0.71069 A |
| Crystal system | MONOCLINIC |
| Space group | P21/c |
| Unit cell dimensions | $a=6.9710(10) \mathrm{A} \quad \alpha=90 \mathrm{deg}$. |
|  | $\mathrm{b}=14.5330(10) \mathrm{A} \quad \beta=92.417$ (11) |
|  | $\mathrm{c}=14.2530(10) \mathrm{A} \quad \gamma=90 \mathrm{deg}$. |
| Volume | 1442.7(3) $\mathrm{A}^{3}$ |
| Z | 4 |
| Denisty (calculated) | $2.363 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $9.418 \mathrm{~mm}^{-1}$ |
| F(000) | 964 |
| Crystal size | $0.33 \times 0.08 \times 0.04 \mathrm{~mm}$ |
| Theta range for data collection | 2.00 to 25.01 deg . |
| Index ranges | $-5<=\mathrm{h}<=7,-16<=\mathrm{k}<=15,-14<=1<=15$ |
| Reflections collected | 6138 |
| Independent reflections | 2177 [ $\mathrm{R}(\mathrm{int})=0.1150]$ |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2177/0/227 |
| Goodness-on-fit $\mathrm{F}^{2}$ | 0.638 |
| Final R indices [ $1>2 \mathrm{sigma}(1)$ ] | $\mathrm{RI}=0.0380 . w \mathrm{R} 2=0.09 \mathrm{ll}$ |
| R indices (all data) | $\mathrm{Rl}=0.0457, \mathrm{wR2}=0.0947$ |
| Largest diff. Peak and hole | 2.290 and $-1.133 \mathrm{e} . \mathrm{A}^{-3}$ |

## 2- Preparation of Trans-(Dimethylsulfoxide)-diiodo(2methylpyridine) platinum(II), trans-[Pt(2-Mepy)(DMSO)I $\left.{ }_{2}\right]$ (D):

This complex was prepared by a method similar to the literature procedure [Ha, et al., (1990)]. cis-Diiodo-bis(2-methylpyridine) platinum(II) (C) $(0.127 \mathrm{~g}, 0.2 \mathrm{mmol})$ was dissolved in dimethylsulfoxide ( $60 \mathrm{ml}, 768 \mathrm{mmol}$ ). The excess of dimethylsulphoxide and the dissociated 2 -methylpyridine were removed by distillation under vacuum. The orange product was dried and recrystallized from chloroform to give trans-[Pt(2-Mepy)(DMSO)I ${ }_{2}$ ] ( $0.09 \mathrm{~g}, 69 \%$ yield). Anal. Calcd. for $\mathrm{C}_{8} \mathrm{H}_{13} \mathrm{NSOL}_{2}$ Pt: $\mathrm{C}, 15.49 ; \mathrm{H}, 2.10 ; \mathrm{N}, 2.25 \%$. Found: C, 15.7; H, 2.2; N, $2.3 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(360 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)(\delta \mathrm{ppm})$ shown as (Fig. 1). $8.60(1 \mathrm{H}$, d, J=4.8 Hz, J $\left.\mathrm{J}_{\mathrm{P} \cdot \mathrm{H}}=33 \mathrm{~Hz}, \mathrm{H}_{0}\right) ; 7.66\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=7.7,7.7 \mathrm{~Hz}, \mathrm{H}_{\mathrm{p}}\right) ; 7.33(1 \mathrm{H}$, d, $\left.J=7.5 \mathrm{~Hz}, \mathrm{H}_{\mathrm{m} 1}\right) ; 7.21\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=6.3,6.2 \mathrm{~Hz}, \mathrm{H}_{\mathrm{m} 2}\right) ; 3.86\left(6 \mathrm{H}, \mathrm{s}, \mathrm{J}_{\mathrm{p} 1}\right.$. $\mathrm{H}=21.7 \mathrm{~Hz}, 2 \mathrm{CH}_{3}$ groups of DMSO); $2.97\left(3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right.$ group of 2methylpyridine).

## ${ }^{1}$ H NMR Measurement:

A solution of (A) ( $6.3 \times 10^{-2} \mathrm{M}$ ) in DMSO-d6 gave two sets of equivalent signals (Fig. 2) due to dispiacement of one nitrate group by DMSO-d6 and the consequent formation of (B), 1:1 $\left[\mathrm{Pt}(\right.$ bipy $)\left(\mathrm{ONO}_{2}\right)$ (DMSO) $\mathrm{NO}_{3} .{ }^{1} \mathrm{H}$ NMR ( $360 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}$ ) ( $\left.\delta \mathrm{ppm}\right) 9.29(1 \mathrm{H}, \mathrm{d}$, $\left.\left.J=5.8 \mathrm{~Hz}, \mathrm{H}_{6}\right) ; 8.82\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=8.1 \mathrm{~Hz}, \mathrm{H}_{6}\right)^{\prime}\right) ; 8.77\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=7.82 \mathrm{~Hz}, \mathrm{H}_{3}\right)$; $8.60\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=7.9,6.4 \mathrm{~Hz}, \mathrm{H}_{4}\right) ; 8.57\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=6.5,7.9 \mathrm{~Hz}, \mathrm{H}_{4}\right) ; 8.50$ $\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5.8 \mathrm{~Hz}, \mathrm{H}_{3}{ }^{\prime}\right) ; 8.05\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=6.4,7.0 \mathrm{~Hz}, \mathrm{H}_{5}\right) ; 7.99(1 \mathrm{H}, \mathrm{dd}$, $\left.\mathrm{J}=6.3,6.4 \mathrm{~Hz}, \mathrm{H}_{\mathrm{s}}{ }^{\prime}\right) ; 3.45\left(6 \mathrm{H}, \mathrm{s}, 2 \mathrm{CH}_{3}\right.$ groups of DMSO-d6).

Similar displacement of 2-methylpyridine in cis-[Pt(2-Mepy) $\left.)_{2} \mathrm{I}_{2}\right]$ (C), with DMSO-d $\mathrm{d}_{6}$ was observed by ${ }^{3} \mathrm{H}$ NMR ( 360 MHz ). A solution of (C), $\left(2.5 \times 10^{-2} \mathrm{M}\right)$ in DMSO-d6 gave two sets of equivalent signals due to displacement of one 2 -methylpyridine by DMSO- $\mathrm{d}_{6}$. The signals of the coordinated 2-methylpyridine appeared at lower magnetic field than those for the free ligand. The summary of the ${ }^{1} H$ NMR spectrum is, in effect, the sum of the spectrum of (D) (Fig. 1) and that of 2 -methylpyridine in DMSO- $\mathrm{d}_{6}$ ( F denotes the free ligand whereas L denotes coordinated ligand). ${ }^{1} \mathrm{H}$ NMR ( 360 MHz, DMSO- $\mathrm{d}_{6}$ ) ( $\delta \mathrm{ppm}$ ) $8.60(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=5.8$ $\left.\mathrm{Hz}, \mathrm{H}_{0}(\mathrm{~L})\right) ; 8.43\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=2.8 \mathrm{~Hz}, \mathrm{H}_{0}(\mathrm{~F})\right) ; 7.86(\mathrm{HH}, \mathrm{dd}, \mathrm{J}=7.7 \mathrm{~Hz}$, $\left.H_{p}(\mathrm{~L})\right) ; 7.67\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=7.5,7.6 \mathrm{~Hz}, \mathrm{H}_{\mathrm{p}}(\mathrm{F})\right) ; 7.58(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=7.8 \mathrm{~Hz}$, $\left.\mathrm{H}_{\mathrm{m} 1}(\mathrm{~L})\right) ; 7.40\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=6.6,6.7 \mathrm{~Hz}, \mathrm{H}_{\mathrm{m} 2}(\mathrm{~L})\right) ; 7.25(1 \mathrm{H}, \mathrm{d}, J=7.7 \mathrm{~Hz}$,
$\left.\mathrm{H}_{\mathrm{m} 1}(\mathrm{~F})\right) ; 7.18\left(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=5.4,6.9 \mathrm{~Hz}, \mathrm{H}_{\mathrm{m} 2}(\mathrm{~F})\right) ; 2.88\left(3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right.$ group of (L)); $2.48\left(3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right.$ group of (F)).

An independent measurement of the spectrum of 2-methylpyridine in DMSO-d ${ }_{6}$ showed that the chemical shifts marked $\mathbf{F}$ were correctly assigned to the displaced ligand. Further, the newly coordinated DMSO manifested $\mathrm{J}_{\mathrm{P}-\mathrm{H}}$ of 21.6 Hz .


Fig. (1): $360 \mathrm{MHz}{ }^{1} \mathrm{H}$ NMR spectrum of trans-[Pt(2-Mepy)
(DMSO) $\mathrm{I}_{2}$ ( D ) in $\mathrm{CDCl}_{3}$.


Fig. (2): $360 \mathrm{MHz}{ }^{1} \mathrm{H}$ NMR spectrum of $\left[\operatorname{Pt}(\right.$ bipy $\left.)\left(\mathrm{NO}_{3}\right)_{2}\right]$
(A) in DMSO-d ${ }_{6}$

## RESULTS AND DISCUSSION

The IR spectrum of the solid compound $\left[\mathrm{Pt}(\right.$ bipy $\left.)\left(\mathrm{NO}_{3}\right)_{2}\right]$ (A), which is crystallized from aqueous acetone, shows a strong absorption band at $1715 \mathrm{~cm}^{-1}$ due to the carbonyl stretching mode, vCO , of the solvent of crystallization. This band disappears on warming, when the acetone is lost. The crystal structure (Fig. 3) shows the acetone interspersed between the molecules containing 4 -coordinated platinum(II).


Fig. (3): View of the unit cell along a-axis of $\left[\mathrm{Pt}(\right.$ bipy $\left.)\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot 0.5\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$

The nitrate conformations (Fig. 4) call for comment. The homoleptic $\left[\mathrm{Pt}\left(\mathrm{ONO}_{2}\right)_{4}\right]^{2 \cdot}$ ion in its monohydrated salt with potassium, $\mathrm{K}_{2}\left[\left(\mathrm{PtONO}_{2}\right)_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, has all 4 unidentate Pt-O (201 pm) nitrate ligands disposed to one side of the metal ion, forming a "basket" conformation [Elding \& Oskarsson (1985)]. The secondary Pt-O vectors are 299 pm . The present situation is similar, with, in effect, the planar 2,2'-bipyridyl replacing 2 of the cis-nitrate ligands in $\left[\mathrm{Pt}\left(\mathrm{ONO}_{2}\right)_{4}\right]^{2-}$. The conformation of the cis-dinitrato-fragment is close to that in the tetrakis-species.


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Fig. (4):The conformations of the coordinated nitrate ligands in $\left[\mathrm{Pt}(\right.$ bipy $\left.)\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot 0 \cdot 5\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}(\mathrm{A})$.

The study [Canty et al., (1992)] of single crystals of the compound $\left[\mathrm{Pd}(\right.$ bipy $\left.) \mathrm{Cl}_{2}\right]$ prompts us to comment. The compound is known [Bielli et al., (1974) and Canty et al., (1992)] to be isomorphous with its platinum eutrope (the yellow dimorph). Further, although the latest work found single crystals of the yellow form of $\left[\mathrm{Pt}(\right.$ bipy $) \mathrm{Cl}_{2}$ ] difficult to obtain, the structure of such single crystals had actually been studied [Idem, unpublished research (1975) and Textor \& Oswald (1974)].

The reported coordinates [Textor \& Oswald (1974)] for platinum ( $\mathrm{x}, \mathrm{y}$ and $\mathrm{z}, 0.17,0.30$ and $0.625 \AA$ ) correspond to those in a further study [Idem, unpublished research (1975)] ( $0.1686,0.3023$ and $0.6220 \AA$ ). In both dimorphs, the planar molecules are arranged in stacks. In the red form, the platinum atoms lie almost directly above each other (with $\mathrm{Pt}-\mathrm{Pt}$ $3.45 \AA$ [Textor \& Oswald (1974)]), $4.54 \AA$ [Idem, unpublished research (1975)] (cf. for Pd-Pd $4.587 \AA$ [Canty et al., (1992)]). The molecules for the yellow form are slewed in their own planes and translated in both the palladium [Canty et al., (1992)] and the platinum [Idem, unpublished research (1975) and Textor \& Oswald (1974)] compounds

On dissolution in DMSO, the uncharged (A) forms a conducting solution, indicating solvolysis to charged species, as in equation (1).

The ${ }^{1} H$ NMR spectrum of the solution indicates that the two-fold symmetry element of (A) relating to the two halves of the bipyridyl ligand has been lost. The signals for each type of proton (at positions 3, 4, 5 and 6 of the ligand) split into two (for $3,3^{\prime} ; 4,4^{\prime} ; \ldots$ etc.).

The rate of exchange of bulk (solvent) DMSO with coordinated DMSO seems high, since no coupling of the platinum-195 nuclei to it is seen. This contrasts with the compound trans-diiodo- $(S$-DMSO $)(2$ methylpyridine)platinum(II) (D), in $\mathrm{CDCl}_{3}$, (Fig. 2), where a clear coupling is evident ( $\mathrm{J}_{\mathrm{Pt}-\mathrm{H}} 21.6 \mathrm{~Hz}$ ). A smaller coupling ( $\mathrm{J}_{\mathrm{P}-\mathrm{H} \cdot \mathrm{Ca}} .12 \mathrm{~Hz}$ ) is also evident in (D) for the proton of 2-methylpyridine at the 6-position, adjacent to the ligated nitrogen.

Table (2): Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent Isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{C}_{12.5} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6.5} \mathrm{Pt}$. $U(e q)$ is defined as one third of the trace of the orthogonalized Uij tensor.

|  | $x$ | $y$ | $z$ | U(eq) |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |
| $\mathrm{Ptt}(1)$ | $1507(1)$ | $860(1)$ | $3785(1)$ | $34(1)$ |
| $\mathrm{O}(1)$ | $562(9)$ | $1074(4)$ | $2431(4)$ | $50(2)$ |
| $\mathrm{O}(2)$ | $3065(14)$ | $1893(8)$ | $2210(7)$ | $128(4)$ |
| $\mathrm{O}(3)$ | $988(11)$ | $1686(5)$ | $1093(5)$ | $75(2)$ |
| $\mathrm{O}(4)$ | $692(8)$ | $2174(4)$ | $4049(4)$ | $49(1)$ |
| $\mathrm{O}(5)$ | $3681(11)$ | $2601(5)$ | $4216(7)$ | $81(2)$ |
| $\mathrm{O}(6)$ | $1413(10)$ | $3619(4)$ | $3932(4)$ | $69(2)$ |
| $\mathrm{N}(1)$ | $2289(8)$ | $502(5)$ | $5101(4)$ | $37(2)$ |
| $\mathrm{N}(2)$ | $2054(9)$ | $-460(4)$ | $3569(4)$ | $34(1)$ |
| $\mathrm{N}(3)$ | $1984(12)$ | $2833(5)$ | $4049(5)$ | $52(2)$ |
| $\mathrm{N}(4)$ | $1600(12)$ | $1568(5)$ | $1884(6)$ | $54(2)$ |
| $\mathrm{C}(1)$ | $2368(12)$ | $1079(6)$ | $5848(6)$ | $44(2)$ |
| $\mathrm{C}(2)$ | $2921(13)$ | $767(6)$ | $6722(6)$ | $50(2)$ |
| $\mathrm{C}(3)$ | $3419(11)$ | $-125(7)$ | $6865(6)$ | $51(2)$ |
| $\mathrm{C}(4)$ | $3344(12)$ | $-725(6)$ | $6086(6)$ | $48(2)$ |
| $\mathrm{C}(5)$ | $2772(10)$ | $-392(5)$ | $5223(5)$ | $36(2)$ |
| $\mathrm{C}(6)$ | $2624(11)$ | $-941(5)$ | $4352(6)$ | $37(2)$ |
| $\mathrm{C}(7)$ | $2986(12)$ | $-1883(6)$ | $4297(7)$ | $51(2)$ |
| $\mathrm{C}(8)$ | $2804(13)$ | $-2319(6)$ | $3434(7)$ | $56(2)$ |
| $\mathrm{C}(9)$ | $2243(13)$ | $-1819(6)$ | $2667(7)$ | $61(3)$ |
| $\mathrm{C}(10)$ | $1876(13)$ | $-883(5)$ | $2750(7)$ | $46(2)$ |
| $\mathrm{O}(111)$ | $4690(28)$ | $4609(18)$ | $6115(13)$ | $112(7)$ |
| $\mathrm{C}(110)$ | $6736(32)$ | $4539(15)$ | $4956(17)$ | $137(6)$ |
| $\mathrm{C}(111)$ | $3433(380)$ | $5445(144)$ | $4854(210)$ | $1618(206)$ |
| $\mathrm{C}(112)$ | $4775(48)$ | $4885(19)$ | $5341(15)$ | $89(10)$ |

The substitution of 2 -methylpyridine(2-picoline) in $\mathbf{C}$, cis-[ $\mathrm{Pt}(2-$ Mepy $\left.)_{2} \mathrm{I}_{2}\right]$ with DMSO- $\mathrm{d}_{6}$ to (D), trans-[Pt(2-Mepy)(DMSO-d6) $\left.\mathrm{I}_{2}\right]$, took place in two steps according to ref. 1. Iodide first substitutes DMSO- $\mathrm{d}_{6}$ to give $\left[\mathrm{Pt}(2-\mathrm{Mepy})\left(\mathrm{DMSO}-\mathrm{d}_{6}\right) \mathrm{I}_{2}\right]+2$-Mepy (in the solution). In our present system, with $\mathrm{N}, \mathrm{N}^{\prime}$-chelated 2,2'-bipyridyl rather than unidentate 2 picoline, stereochange (cis-trans) is prevented.

Table (3): Bond Length $\left[\AA\right.$ ] and Angles [ ${ }^{\circ}$ ] for $\mathrm{C}_{12.5} \mathrm{H}_{9} \mathrm{~N}_{4} \mathrm{O}_{6.5} \mathrm{Pt}$.

| $\mathrm{Pt}(1)-\mathrm{N}(2)$ | $1.983(7)$ |
| :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{N}(1)$ | $1.999(6)$ |
| $\mathrm{Pt}(1)-\mathrm{O}(4)$ | $2.031(5)$ |
| $\mathrm{Pt}(1)-\mathrm{O}(1)$ | $2.036(6)$ |
| $\mathrm{O}(1)-\mathrm{N}(4)$ | $1.303(9)$ |
| $\mathrm{O}(2)-\mathrm{N}(4)$ | $1.202(11)$ |
| $\mathrm{O}(3)-\mathrm{N}(4)$ | $1.200(10)$ |
| $\mathrm{O}(4)-\mathrm{N}(3)$ | $1.316(9)$ |
| $\mathrm{O}(5)-\mathrm{N}(3)$ | $1.243(10)$ |
| $\mathrm{O}(6)-\mathrm{N}(3)$ | $1.219(10)$ |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | $1.353(10)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1.354(11)$ |
| $\mathrm{N}(2)-\mathrm{C}(10)$ | $1.321(11)$ |
| $\mathrm{N}(2)-\mathrm{C}(6)$ | $1.362(10)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.366(13)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.356(12)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | $1.411(12)$ |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | $1.365(11)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | $1.476(12)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | $1.395(11)$ |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | $1.385(12)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | $1.357(13)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | $1.391(11)$ |
| $\mathrm{O}(111)-\mathrm{C}(112)$ | $1.18(2)$ |
| $\mathrm{C}(110)-\mathrm{C}(112)$ | $1.58(4)$ |
| $\mathrm{C}(111)-\mathrm{C}(112)$ | $1.40(4)$ |
| $\mathrm{N}(2)-\mathrm{Pt}(1)-\mathrm{N}(1)$ | $81.2(3)$ |
| $\mathrm{N}(2)-\mathrm{Pt}(1)-\mathrm{O}(4)$ | $174.4(2)$ |
| $\mathrm{N}(1)-\mathrm{Pt}(1)-\mathrm{O}(4)$ | $97.9(3)$ |
| $\mathrm{N}(2)-\mathrm{Pt}(1)-\mathrm{O}(1)$ | $93.3(3)$ |
| $\mathrm{N}(1)-\mathrm{Pt}(1)-\mathrm{O}(1)$ | $173.1(2)$ |
| $\mathrm{O}(4)-\mathrm{Pt}(1)-\mathrm{O}(1)$ | $87.2(2)$ |
| $\mathrm{N}(4)-\mathrm{O}(1)-\mathrm{Pt}(1)$ | $119.1(5)$ |
| $\mathrm{N}(3)-\mathrm{O}(4)-\mathrm{Pt}(1)$ | $119.2(5)$ |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(1)$ | $119.4(7)$ |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Pt}(1)$ | $115.3(5)$ |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{Pt}(1)$ | $125.2(6)$ |
|  |  |


| $\mathrm{C}(10)-\mathrm{N}(2)-\mathrm{C}(6)$ | $119.9(7)$ |
| :--- | :--- |
| $\mathrm{C}(10)-\mathrm{N}(2)-\mathrm{Pt}(1)$ | $125.2(6)$ |
| $\mathrm{C}(6)-\mathrm{N}(2)-\mathrm{Pt}(1)$ | $114.9(5)$ |
| $\mathrm{O}(6)-\mathrm{N}(3)-\mathrm{O}(5)$ | $125.7(8)$ |
| $\mathrm{O}(6)-\mathrm{N}(3)-\mathrm{O}(4)$ | $117.6(8)$ |
| $\mathrm{O}(5)-\mathrm{N}(3)-\mathrm{O}(4)$ | $116.6(7)$ |
| $\mathrm{O}(3)-\mathrm{N}(4)-\mathrm{O}(2)$ | $124.7(9)$ |
| $\mathrm{O}(3)-\mathrm{N}(4)-\mathrm{O}(1)$ | $117.2(8)$ |
| $\mathrm{O}(2)-\mathrm{N}(4)-\mathrm{O}(1)$ | $118.0(8)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $120.8(8)$ |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | $121.0(8)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | $118.2(8)$ |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | $119.3(8)$ |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | $121.2(8)$ |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | $113.7(7)$ |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | $125.0(8)$ |
| $\mathrm{N}(2)-\mathrm{C}(6)-\mathrm{C}(7)$ | $120.3(8)$ |
| $\mathrm{N}(2)-\mathrm{C}(6)-\mathrm{C}(5)$ | $114.8(6)$ |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | $124.8(8)$ |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | $119.3(8)$ |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | $118.9(8)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | $120.3(9)$ |
| $\mathrm{N}(2)-\mathrm{C}(10)-\mathrm{C}(9)$ | $121.3(9)$ |
| $\mathrm{O}(111)-\mathrm{C}(112)-\mathrm{C}(110)$ | $107(3)$ |
| $\mathrm{O}(111)-\mathrm{C}(112)-\mathrm{C}(111)$ | $127(10)$ |
| $\mathrm{C}(110)-\mathrm{C}(112)-\mathrm{C}(111)$ | $126(10)$ |

Symmetry transformations used to generate equivalent atoms: \#-$x+1,-y+1,-z+1$

The reactivity toward nucleophiles of compounds where aromatic N -heterocycles are coordinated to platinum(II) often seems anomalously high by comparison with alicyclic or aliphatic analogues: $\left[\mathrm{Pt}(\text { bipy })_{2}\right]^{2+}$ forms 1:1 adducts with several sulphur-nucleophiles [Wernberg (1986)] $\left(\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right.$, thiourea) and with hydroxide, [Gillard $\&$ Lyon (1973)] and $\left[\mathrm{Pt}(\right.$ bipy $\left.) \mathrm{Cl}_{2}\right]$ reacts readily with pentasulphide, $\mid \mathrm{Collins}$ et al. (1993) and Gameiro et al., (2001)] which unexpectedly displaces the N -heterocycle, forming the $\left[\mathrm{Pt}\left(\mathrm{S}_{5}\right)_{3}\right]^{2-}$ ion. The reaction here with DMSO may well involve its nuleophilic attack via the sulphur centre. In view of the
common use of DMSO- $\mathrm{d}_{6}$ as a solvent for NMR work on the complex ions, it is worth emphasizing that, although aprotic, it is often a good nucleophile for metal ions of class (b). As in the present case, solvolysis may be appreciable.

Table (4):Anisotropic Displacement Parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{C}_{12}{ }_{5} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{Pt}$ The anisotropic displacement factor exponent takes the form: -2 pi^2[h^2a*^2 U11 + ... $\left.+2 \mathrm{~h} k \mathrm{a}^{*} \mathrm{~b}^{*} U 12\right]$

|  | U11 | U22 | U33 | U23 | U13 | U12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)$ | $33(1)$ | 32(1) | 35(1) | 3(1) | 2(1) | -I(1) |
| $\mathrm{O}(1)$ | $51(4)$ | 61(t) | 36(3) | 11(3) | -4(3) | -6(3) |
| $\mathrm{O}(2)$ | 103(7) | 202(11) | 79(6) | 41 (6) | 5(5) | -78(7) |
| O(3) | 110(6) | 81(5) | $36(4)$ | 18(3) | 1 (4) | $11(+)$ |
| $\mathrm{O}(4)$ | 46(3) | 36(3) | $66(4)$ | 4 (3) | 1 (3) | 7(3) |
| O(5) | $61(5)$ | 60(5) | 123(7) | -5(4) | $4(4)$ | -14(4) |
| O (6) | 113(6) | 28(4) | 66(5) | 3(3) | -6(4) | 13(3) |
| $\mathrm{N}(1)$ | $31(3)$ | $50(4)$ | 30(4) | $8(3)$ | 2(3) | -3(3) |
| $\mathrm{N}(2)$ | 36(3) | 34(4) | $31(4)$ | 3(3) | -1(3) | -7(3) |
| $\mathrm{N}(3)$ | 69(6) | $41(5)$ | 45(4) | -3(3) | 1(4) | -8(t) |
| $\mathrm{N}(4)$ | 68(5) | 46(4) | 50(5) | $5(4)$ | $10(4)$ | -10(4) |
| C(1) | 43 (5) | 51(5) | $38(5)$ | -8(4) | $9(4)$ | -7(4) |
| $\mathrm{C}(2)$ | +6(5) | 68(7) | 37(5) | -2(4) | 4(4) | -9(4) |
| C(3) | $39(5)$ | $80(7)$ | 33(5) | 15 (5) | -4(3) | -10(4) |
| C(4) | 37(6) | 39(5) | 47(6) | 12(4) | $5(4)$ | -10(3) |
| C(5) | $29(+)$ | 39(5) | 41(5) | 10(4) | 5 (3) | -1(3) |
| C(6) | $22(4)$ | +1(5) | 49 (5) | 1(4) | 4(3) | -2(3) |
| C(7) | $51(5)$ | 39(5) | $61(6)$ | $8(4)$ | $-3(4)$ | -2(4) |
| $\mathrm{C}(8)$ | $67(6)$ | $33(5)$ | 67(6) | -2(5) | -2(5) | 4(4) |
| $\mathrm{C}(9)$ | $65(6)$ | 61 (6) | $57(6)$ | -28(5) | $5(5)$ | -14(5) |
| C(10) | +4(5) | 41 (5) | 52(6) | 2(4) | $6(4)$ | -4(3) |
| $\mathrm{O}(111)$ | 102(14) | 157(19) | 75(13) | $35(13)$ | -17(10) | -56(14) |
| C(110) | 151(18) | 102(1+) | 159(18) | 1(14) | 24(15) | -4(13) |
| C(111) | 1482(631) | $1281(399)$ | 2000(298) | $-74+(369)$ | -1000(513) | $440(268)$ |
| $\mathrm{C}(112)$ | 1+8(25) | 85(19) | 31(12) | 32(11) | -18(12) | -81(19) |

Table (5): Hydrogen Coordinates ( $\times 10^{4}$ ) and Isotropic
Displacement Parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{C}_{12.5} \mathrm{H}_{8} \mathrm{~N}_{4} \mathrm{O}_{6.5} \mathrm{Pt}$.

|  | $x$ | $y$ | $z$ | $U($ iso $)$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{H}(1)$ | $2042(12)$ | $1695(6)$ | $5764(6)$ | $64(10)$ |
| $\mathrm{H}(2)$ | $2957(13)$ | $1174(6)$ | $7226(6)$ | $64(10)$ |
| $\mathrm{H}(3)$ | $3799(11)$ | $-336(7)$ | $7460(6)$ | $64(10)$ |
| $\mathrm{H}(4)$ | $3682(12)$ | $-1341(6)$ | $6159(6)$ | $64(10)$ |
| $\mathrm{H}(7)$ | $3345(12)$ | $-2215(6)$ | $4834(7)$ | $64(10)$ |
| $\mathrm{H}(8)$ | $3062(13)$ | $-2945(6)$ | $3382(7)$ | $64(10)$ |
| $\mathrm{H}(9)$ | $2102(13)$ | $-2104(6)$ | $2984(7)$ | $64(10)$ |
| $\mathrm{H}(10)$ | $1499(13)$ | $-548(5)$ | $2218(7)$ | $64(10)$ |

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## التركيب البلودى للمترّاكب ثنـائى نيتراتو Y ، Y باى بيريدين للأتنيوم وتحلله

تم فى هذا البحث در اسية التُركيب البلور ى للمتر اكب المذكور فى عنوان البحث وذلك
 المنناطيسى المّيلروجينى وكالثك بالتُوصبِل الكهربى. . cis-[Pt(2-methylpyridine $)_{2} \mathrm{I}_{2}[$ كما تم دراسة تُحلا المتّر اكبا

