Isomers of Platinum(II) and Palladium(II) Complexes

PREDICTING THE DIRECTION OF ISOMERISATION AND RELATIVE THERMODYNAMIC STABILITY

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Geometrical isomers of platinum(II) and palladium(II) differ substantially in their chemical and biological properties. Under certain conditions one isomeric compound can transform into another. It is essential for chemists to be aware of the probable direction of the isomerisation process, and to predict which isomer is likely to be relatively more stable. The rules in this paper will permit such judgements to be made.

Complex compounds of platinum(II) have played an important part in the formation and development of co-ordination theory, and this has given a strong impetus to the growth of inorganic chemistry. The existence of two isomeric forms for the PtX_2A_2 compounds (where A is amine, and X is anion) allowed Werner to conclude that platinum(II) complexes have square-planar structures (1). These isomeric forms are a result of the *cis*- and *trans*- locations of ligands A and X.
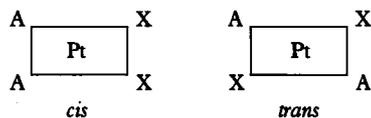
Later, the conclusion about the square-planar structure of platinum(II) complexes was repeatedly confirmed by various physical and chemical methods of investigation.

Isomeric compounds of platinum(II) differ significantly in their reactivities, and many of the chemical methods used for the identification of individual forms are based on this (2). Different rates of substitution of ligands often result in a substantial difference in the catalytic properties of two isomeric complexes. A remarkable discovery was made twenty years ago when it was found that *cis*-[PtCl$_2$(NH$_3$)$_2$] had clearly pronounced anti-cancer properties, while its *trans*-isomer was completely inactive (3,4). The same

picture could be observed for other diaminedihalogen complexes of platinum(II). This discovery was used as a basis for a perceived application in medicine; namely the use of co-ordination compounds for the chemical treatment of cancer.

Isomeric compounds are often different in their thermodynamic stabilities. Thus, Chernyaev and his co-workers established that the total energy of *trans*-[PtCl$_2$(NH$_3$)$_2$] is about 13 kJ/mol less than that of the *cis*-isomer (5). Thus, under certain conditions, it can be expected that *cis*-[PtCl$_2$(NH$_3$)$_2$] will undergo isomerisation into *trans*-[PtCl$_2$(NH$_3$)$_2$]. The existence of isolable isomeric pairs is caused by the inertness of platinum(II) complexes. Square-planar complexes of nickel(II) are more labile than platinum(II) complexes; for this reason, *cis*- and *trans*-isomeric pairs are almost unknown for nickel(II) complexes. Palladium(II) complexes have intermediate lability. Therefore, isomeric *cis*- and *trans*-pairs of palladium(II) are fewer in number than for platinum(II), but are more numerous than for nickel(II).

Experimental evidence shows that the isomeric complexes of platinum(II) and palladium(II) interconvert, often spontaneously or in the presence of catalytic agents. Sometimes, *trans*-configuration complexes transform to their respective *cis*-configuration complexes, but more

frequently this occurs the other way round, that is the *cis*-form being less stable converts to the *trans*-form. These conversions can be observed both in the solid phase and in solution. For example, the complex [PtBr$_2$(NH$_3$)$_2$] isomerises into *trans*-[PtBr$_2$(NH$_3$)$_2$] at 250°C (6), while with *trans*-[PtCl$_2$py(Et$_2$SO)] (where py is pyridine and Et is ethyl), the reverse takes place, and it isomerises into *cis*-[PtCl$_2$py(Et$_2$SO)] at 134°C (7).

Predicting the direction of isomerisation is very important for chemists. If such a prediction can be made, then the relative thermodynamic stabilities can be predicted simultaneously for individual isomeric complexes.

Different approaches can be used to explain the direction of isomerisation. Many facts about the isomerisation of platinum(II) and palladium(II) complexes have been considered by the author with regard to the *trans*-effect of the ligands (2). As a result, a substantial amount of experimental data has been explained and the direction predicted for yet unknown isomerisation processes (8, 9).
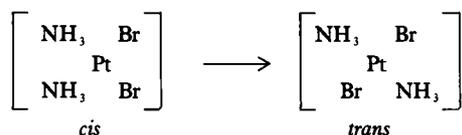
The *trans*-effect phenomenon has kinetic and static aspects. In a study of the kinetic and static aspects of the phenomenon, two respective series of ligands are obtained.

Since isomerisation is connected with the dynamic side of the said phenomenon, then for the most common ligands the *trans*-effect series can be written as follows: H$_2$O < NH$_3$, amines < Cl$^-$ < Br$^-$ < NO$^-_2$ < PR$_3$, R$_2$SO < CO < CR$^-_3$. It should be noted that ligands are arranged in order of increasing *trans*-effect. The more to the right a ligand is in the *trans*-effects row, the greater its lability-producing action will be.

In order to predict the direction of geometric isomerisation for platinum(II) and palladium(II) complexes, it is necessary to select a neutral ligand with the lowest *trans*-effect to use as an indicator. The isomerisation goes in the direction which results in the formation of a complex where that ligand will be located opposite another ligand with the smallest *trans*-effect. If, in the complex in question, the indicator ligand is located opposite a ligand with the next smallest
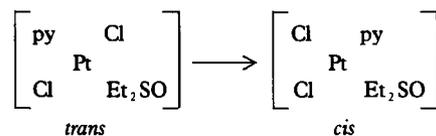
trans-effect, then such a compound should not isomerise.

As was noted above, the following process takes place in the solid phase at 250°C:

$$\begin{bmatrix} NH_3 & Br \\ & Pt \\ NH_3 & Br \end{bmatrix} \longrightarrow \begin{bmatrix} NH_3 & Br \\ & Pt \\ Br & NH_3 \end{bmatrix}$$
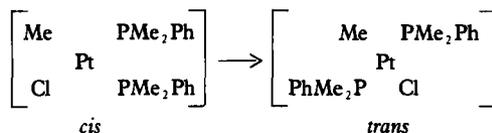$$\quad\quad cis \quad\quad\quad\quad\quad\quad\quad trans$$

In the intial compound, the ammonia molecule has the lowest *trans*-effect and the bromide ion has the greatest. Thus, in the initial compound, both of the ammonia molecules will be prone to isomerisation. Isomerisation takes place in the direction of formation of the *trans*-[PtBr$_2$(NH$_3$)$_2$] complex wherein the ammonia molecules are located opposite the ligand having the lowest *trans*-effect, (that is *trans* to themselves).

In contrast, *trans*-[PtCl$_2$py(Et$_2$SO)] isomerises into the *cis*-configuration compound:

$$\begin{bmatrix} py & Cl \\ & Pt \\ Cl & Et_2SO \end{bmatrix} \longrightarrow \begin{bmatrix} Cl & py \\ & Pt \\ Cl & Et_2SO \end{bmatrix}$$
$$\quad trans \quad\quad\quad\quad\quad\quad\quad cis$$

In the intial complex the pyridine molecule has the lowest *trans*-effect, while the greatest *trans*-effect is exhibited by the diethyl sulphoxide molecule co-ordinated to platinum(II) by its sulphur atom. Thus, in the initial complex, pyridine is labilised by the *trans* diethyl sulphoxide ligand with its strong *trans*-effect and so isomerisation takes place. The molecule of pyridine in *cis*-[PtCl$_2$py(Et$_2$SO)] is less labile, and this complex happens to be more stable thermodynamically.

Two more examples from numerous experimental results will now be considered. Thus, it has been established that the following process takes place in the solid phase (10):

$$\begin{bmatrix} Me & PMe_2Ph \\ & Pt \\ Cl & PMe_2Ph \end{bmatrix} \longrightarrow \begin{bmatrix} Me & PMe_2Ph \\ & Pt \\ PhMe_2P & Cl \end{bmatrix}$$
$$\quad\quad cis \quad\quad\quad\quad\quad\quad\quad\quad trans$$

Since in these complexes the methyl ligand has the greatest *trans*-effect, the phosphine molecule

is labilised and hence isomerisation occurs. The process occurs in the given direction despite the fact that the other phosphine molecule is moving from the position *trans* to the chloride ligand into a *trans*-position relative to the phosphine ligand, that is from a ligand with relatively low *trans*-effect towards a ligand with a somewhat greater *trans*-effect. The important thing is that the phosphine molecule moves away from the ligand having the greatest *trans*-effect.

It has been established that the use of sulphamic acid to remove two nitro-ligands from the $[Pt(NO_2)_4]^{2-}$ complex in a water medium leads to the formation of *cis*-$[Pt(NO_2)_2(H_2O)_2]$, which would then isomerise into *trans*-$[Pt(NO_2)_2(H_2O)_2]$ (11). Both of these processes are caused by the high *trans*-effect of the nitro-ligand, with isomerisation proceeding in accordance with the rule.

Isomerisation of complexes in the solid state can be clearly demonstrated using differential thermal analysis (DTA) curves. In many cases, isomerisation is accompanied by an exothermic peak, as for example, for *cis*-$[PtBr_2(NH_3)_2]$. Frequently, isomerisation shows on the DTA curve as coupled endo- and exothermic peaks, as for example, for *trans*-$[PtCl_2py(Et_2SO)]$. The endothermic peak corresponds to the melting of the initial complex, while the following exothermic peak reflects two processes: isomerisation of the complex and crystallisation of the isomerisation products from the melt. Identical coupled endo- and exothermic peaks can also be observed during isomerisation of *cis*-$[PtMeCl(PMe_2Ph)_2]$ (10). Thus, the presence of an exothermic peak and, especially, of characteristic coupled endothermic and exothermic peaks (without any change in mass in both cases) can point to the isomerisation process.

Since in many cases, platinum(II) and palladium(II) complexes isomerise without any change in mass, it may be concluded that, in the absence of a solvent, isomerisation proceeds without loss of ligands, that is in an intramolecular manner. Probably, a complex of tetrahedral type is an intermediate in the isomerisation process (2).

Thus, using the rule described, it becomes possible to explain comprehensively the isomerisation processes which take place both in the solid phase and in solution.

A Russian proverb states that: "There are no rules without exceptions", and this rule also has exceptions. In particular, the rule does not describe all of the experimental facts for the isomerisation of $[PtX_2(PR_3)_2]$-type phosphine-halogenide complexes. On the other hand, it is quite possible that this rule holds true not only for platinum(II) and palladium(II) complexes, but also for the square-planar complexes of nickel(II), rhodium(I), iridium(I) and gold(III), that is for complexes with a d^8-electron configuration of the central atom. As was noted previously, the square-planar complexes of nickel(II) are rather labile, and for this reason both *cis*- and *trans*-isomeric forms are extremely unlikely to be encountered for $[NiX_2L_2]$-type compounds. However, if we want to see which of the two possible forms exists, then it will be the particular form in whose direction the isomerisation process should be taking place.

No doubt there are different approaches which could be used to explain the direction of isomerisation processes in square-planar complexes. Thus, Jørgensen has formulated the ligand anti-symbiosis principle which enables a judgement to be made about the relative thermodynamic stability of isomeric complexes (12). However, this principle does not describe all of the known experimental facts, either. For example, in a recent paper it was shown that $[PtCl_2LY]$-type complexes (where L is pyridine and its derivatives, and Y is a ligand with a donor atom of oxygen), always have the form of a *trans*-isomer (13). Such a situation cannot be explained using the anti-symbiosis principles (13). It is worth mentioning that the same experimental facts can, however, be explained by the rule described in this paper.

In conclusion, we must note that in addition to the *trans*-effect of inner-sphere ligands, the nature of the solvent and the steric difficulties created by large ligands can be important factors which sometimes influence isomerisation. Naturally, these could complicate the predictions for the direction of the isomerisation process.

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Magneto-Optical Recording Materials

In 1989 the attention of readers of this Journal was drawn to research work being carried out at the Philips Research Laboratories and at E. I. du Pont de Nemours on layered cobalt and platinum structures, which were considered to have potential for magneto-optical recording. In the same issue an abstract of a paper from the Sony Corporation Research Center describing some magneto-optical properties of ultrathin cobalt/platinum and cobalt/palladium layers, also indicated the potential of these materials for high density recording. Continuing interest was demonstrated during 1990 by further reports from these organisations, and from elsewhere.

Progress continues to be made in the subject, as can be gathered from the recent literature which includes, among others, papers from the three establishments named earlier.

According to a combined paper from the first two establishments, large magnetic anisotropy and coercivity in platinum/cobalt multilayers is dependent on sharp interfaces between the layers. Krypton and xenon are better mass-matched to the platinum sputtering target than argon, and their use results in less energetic bombardment by reflected gas neutrals during the film growth. Thus interfacial mixing of the platinum and cobalt films is reduced, and magnetic properties improved. Another way to reduce the mixing of the platinum and cobalt layers, caused by energetic reflected argon atoms, is to sputter at high pressure; this increases the number of collisions that the atoms make before arriving at the substrate, and so reduces their energy (P. F. Carcia and W. B. Zeper, *IEEE Trans. Magn.*, 1990, **26**, (5), 1703–1705).

A further paper from the Sony Corporation gives a review of previous studies on the magnetic properties of cobalt-platinum and cobalt-palladium systems, before going on to describe and discuss current work on cobalt/platinum and cobalt/palladium multilayers. Magnetic hysteresis of the multilayers, their magneto-optical properties, and the effect of sputtering conditions and underlayers on the coercivity, were considered. With large Kerr rotation at shorter wavelengths, and high resistance to corrosion, ultrathin multilayers of both pairs of materials are considered to be promising candidates for high density magneto-optical recording. An examination of dynamic read/write characteristics of the materials was made, with ultrathin multilayers deposited on photo-polymerisation glass substrates, pre-grooved with $1.6\mu m$ pitch. Carrier-to-noise ratios of 53 and 46 dB, at 780 nm, were seen for cobalt-platinum and cobalt/palladium, respectively. A higher ratio will be achieved by refining the noise level and optimising the disc structure (S. Hashimoto and Y. Ochiai, *J. Magn. Magn. Mater.*, 1990, **88**, (1&2), 211–226).

Osmium and Ruthenium Complexes

Recent work on organic oxidations by osmium and ruthenium oxo complexes has been the subject of review No. 22 in the TMC Literature Highlights series (W. P. Griffith, *Trans. Met. Chem.*, 1990, **15**, (3), 251–256).

The most important osmium oxidant is OsO_4 which, when functioning catalytically, is one of the most effective, selective and efficient organic oxidants. Ruthenium complexes in the higher oxidation states are more powerful oxidants than their osmium analogues. While ruthenium(VI) complexes are mild, effective oxidants, osmium(VI) complexes have virtually no oxidative properties. (71 Refs.)