Structure Elucidation of a Platinum Complex by X-Ray Crystallography

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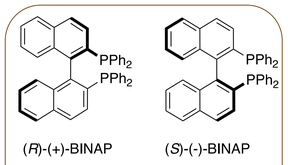
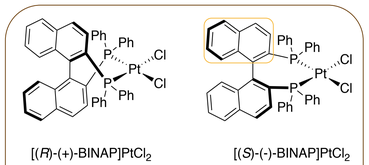
Introduction

- Imagine that you're trying to create a painting, but you can't see where any of the strokes begin or connect. That seems frustrating, even impossible. This is analogous to what synthetic chemistry would be like without the advent of spectroscopic techniques, which allow us to determine the 3-dimensional structures of compounds synthesized in the lab. An example of such a technique is X-ray crystallography. These techniques are crucial as molecule structure directly correlates to function.
- The BINAP ligand shown in Figure 1 is found in many compounds with catalytic, pharmaceutical and industrial properties.[1] It can coordinate with transition metals such as Platinum and Palladium to form complexes such as the one shown in Figure 2, which can lead to unique properties that make these structures useful in stereoselective catalysis and cancer treatments.[2,3]
- In this experiment, X-ray crystallography is used to elucidate the structure of dichloro[2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]platinum(II) or (BINAP)PtCl_2. Knowing the structure of this compound is relevant because it allows scientists interested in testing this compound for similar applications to predict its properties.



(*R*)-(+)-BINAP (*S*)-(-)-BINAP

Figure 1. Structures of BINAP stereoisomers.



[(*R*)-(+)-BINAP]$PtCl_2$ [(*S*)-(-)-BINAP]$PtCl_2$

Figure 2. Lewis structures of (BINAP)$PtCl_2$ supported by BINAP ligands. Highlighted section is called a naphthyl group.

Stereoisomers: What does R and S in Figures 1 and 2 mean?

Chemical compounds can exist in numerous 3-dimensional configurations, even when they're made of the same atoms. This can be thought of as comparing our left and right hands, which are similar but not identical in 3-D space. This type of relationship between molecules is called stereoisomers, and stereoisomers can be distinguished by the R or S designation. The structures in Figure 1 are a specific type of stereoisomer, atropisomer.

Procedure

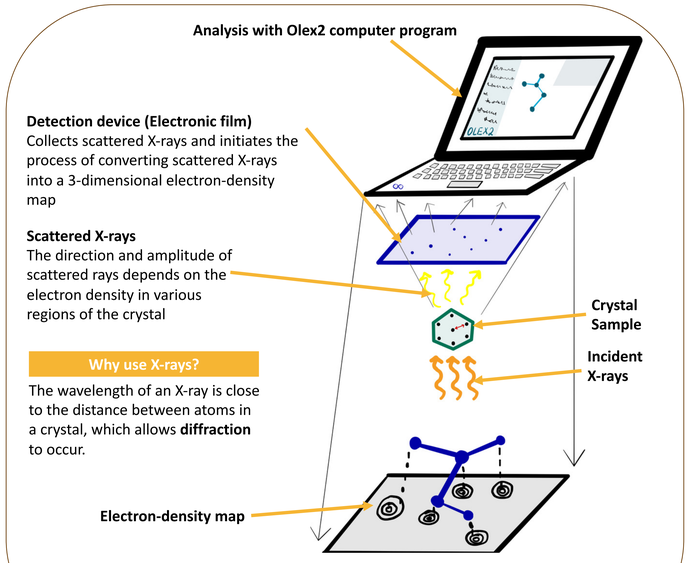


Figure 3. Simplified X-Ray Crystallography setup. X-ray crystallography can be thought of as analogous to light microscopy as it involves the use of electromagnetic radiation (in other words, light) to determine the structure of a material of interest.

Crystal Structure

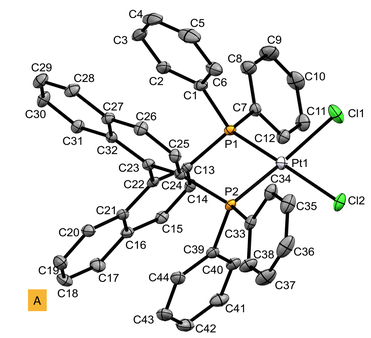


Figure 4. Crystal structure of (BINAP)$PtCl_2$ showing (A) atom labels of the *R* enantiomer (B) close contacts. Phosphorous atoms of BINAP are in yellow, and the Platinum atom is in white. Hydrogen atoms and solvent molecules are omitted for clarity.

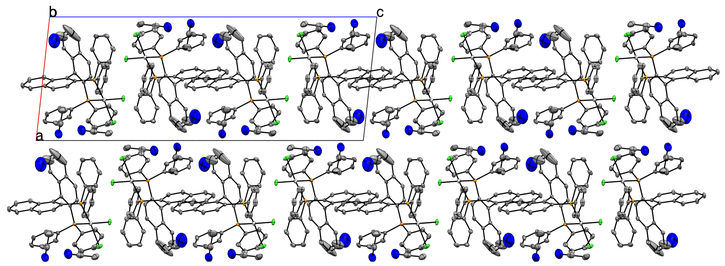


Figure 5. A projection showing the unit cell contents containing both the *R* and *S* enantiomers and the packing of (*rac*BINAP)$PtCl_2$. *rac* stands for racemic, which indicates a mixture of equal amounts R and S stereoisomer.

Bond	Length (Å)
Pt1–Cl2	2.3536(7)
Pt1–P1	2.2448(7)
Pt1–P2	2.2423(8)
P1–C1	1.805(3)
P1–C7	1.825(3)
P1–C13	1.833(3)
P2–C24	1.834(3)
Pt1–Cl1	2.3518(8)

Table 1. Selected bond distances (Å). The numbers in brackets represent error of the measurements.

Bond	Angle (°)
P1–Pt1–Cl2	171.33(3)
Cl2–Pt1–P2	90.62(3)
Cl1–Pt1–Cl2	87.45(3)
P1–Pt1–Cl1	90.31(3)
P2–Pt1–P1	92.86(3)
C12–C7–P1	118.7(2)
C1–P1–C7	106.19(14)
P2–Pt1–Cl1	170.90(3)

Table 2. Selected bond angles (°).

Results and Discussion

- The compound crystalizes in the monoclinic space group $P2_1/c$ – terms used to describe its 3D structure and symmetry – with three acetonitrile solvent molecules present within the asymmetric unit. The solvent molecules have been omitted for clarity. The complex adopts a slightly distorted square-planar geometry about the central Pt(II) atom with *trans* atoms situated at bond angles of ~171º.
- The bidentate BINAP ligand coordinates to Pt with a bite angle (P1–Pt1–P2) of 92.86(3)º, consistent with typical literature values of ~ 93º (Birkholz *et al.*, 2009). This can be clearly seen in Figure 6.
- In a single unit cell (repeating unit that composes the crystal), four independent structures can be observed (Figure 5), with two of each enantiomer depicted in Figure 2 present. Interestingly, no significant intermolecular interactions are present within the sum of van der Walls radii.
- The closest intermolecular interaction stems from hydrogen bonds between neighbouring acetonitrile solvent molecules. These interactions are all greater than 3.40 Å and so were not investigated any further. Distances of ~3.30–3.70 Å can be observed between naphthyl (this is the section of the structure highlighted with a yellow box around it in Figure 2) carbons of neighbouring complexes, however, the arrangement is not stacked and so is likely insignificant.

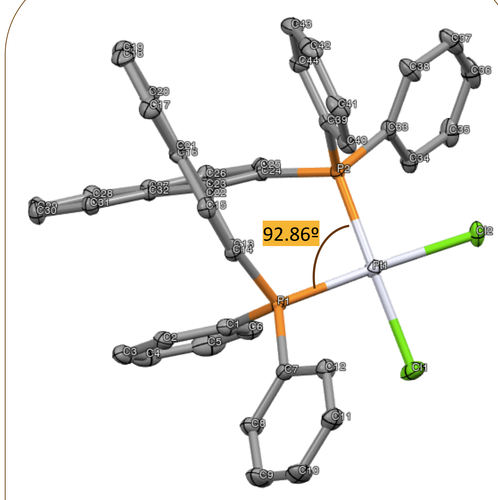


Figure 6. An alternative representation of the R enantiomer showing the bite angle of the bidentate (i.e.: 2 "teeth" or attachments) BINAP ligand coordinating with the Platinum transition metal.

Conclusions

Applications of Similar Compounds

Enantiomeric complexes of the formula $PtCl_2L_2$ including (BINAP)$PtCl_2$ have also been examined for their cytotoxic activity against cancer cell lines and their ability to bind to the human telomeric sequence folded in the G-quadruplex structure (Bombard *et al.*, 2010). Although less cytotoxic than their amine analogues, these complexes are highly active against numerous tumour cell lines, differing significantly in activity based on which enantiomer is present (Bombard *et al.*, 2010). Knowing the structure of this complex would help guide testing of this compound in similar applications.

Key Observations and Comparisons to Previous Literature

- The crystal structure of {(*R*)-BINAP}$PtCl_2$ has been previously reported as a dichloromethane solvate (Doherty *et al.*, 2006). The solid-state structure of the racemic form, [*rac*BINAP]$PtCl_2$ however, has to the best of our knowledge, not been described. The solid-state structure of [*rac*BINAP]$PtCl_2$ obtained by single crystal X-ray diffraction is shown in Figure 4 (*R* enantiomer) and selected bond lengths and angles highlighted in Table 1 and 2.
- In the solid-state, evidence of intramolecular π-stacking between naphthyl and phenyl substituents is observed, generating close contacts ranging from ~3.2–4.0 Å (Figure 4, B).
- The Pt–Cl bond lengths (Pt1–Cl1 = 2.3518(8) Å; Pt1–Cl2 = 2.3536(7) Å) are only ~0.01 Å longer than those in Pd analogue (Véron *et al.*, 2013).
- The two Pt-Cl distances are also statistically indistinguishable, implying similar orbital overlap between the Pt(II) metal centre and the strong *trans* phosphine donors.
- An only slightly acute Cl1–Pt1–Cl2 angle is observed [87.45(3)°], indicating slight steric repulsion from the diphenylphosphine arms.
- The bond lengths involving the Pt metal centre are similar to those in the enantiopure {(*R*)-BINAP}$PtCl_2$ (Doherty *et al.*, 2006), however, deviations are observed in several of the angles. Most notably, the *trans* P–Pt–Cl angles have opened to ~171º in comparison to ~168° in the dichloromethane solvate (Doherty *et al.*, 2006).
- This study provides a structural investigation of this compound and may be useful for guiding the design of future chiral BINAP-based ligands and their Pt complexes.

Future Directions

- It would be useful to compare bond lengths and angle of this crystal structure with similar compounds, perhaps with another transition metal instead of Pt or a variation of the BINAP ligand.
- Other spectroscopic techniques such as NMR, absorption spectra, etc. should also be used to further characterize this compound and determine significant properties that may be compared with the data for compounds mentioned in the previous point.

Acknowledgements

I would like to thank the University of Manitoba and NSERC for the USRA which made this research possible. I would also like to express my gratitude to all members of the Herbert research group for their support.