

Synthesis and Crystal Structure of Tetrachloro(1,10-phenanthroline)platinum(IV)

Robert M. Granger II¹, Jill N. Granger², Kelly del Campo³,
Molly B. Becherer⁴, and Phillip E. Fanwick⁵,

Department of Chemistry, Virginia Military Institute, Lexington VA
and the

Department of Chemistry, Sweet Briar College, Sweet Briar VA.

ABSTRACT

We report the crystal structure determination of tetrachloro(1,10-phenanthroline)platinum(IV). X-ray data indicate there is little steric repulsion between the α -hydrogens on the phenanthroline ligand and the chloride ligands in the equatorial plane.

BACKGROUND

Coordination complexes of the type $M(N-N)_x$, [$M =$ rhodium (Barton, J. K, 1989), (Fleisher, Waterman, Turro & Barton, 1986), (Pyle, Long & Barton, 1989), nickel (Mack & Dervan, 1990), copper (Barton 1986), (Pope, & Sigman 1984) ruthenium or rhodium (Barton, J. K, 1989), (Barton 1986), $N-N = 1,10$ -phenanthroline, its substituted derivatives, or bipyridine and its substituted derivatives], have been used as molecular probes of secondary DNA structure and as indicators of DNA sequence by acting as artificial nucleases. The metal-phenanthroline interaction holds the phenanthroline ligand in a rigid conformation thus allowing for site specific intercalation of the ligand into the DNA. The site specificity and the strength of the interactions are functions of both the substitution on the ligands and the characteristics of the coordinated metal center. An X-ray structural determination of the complex $M(N-N)_x$ allows one to obtain information regarding the three dimensional structure of the site in the DNA to which it binds. Although there have been many studies of DNA interactions with these types of coordination complexes, no studies to date have involved similar octahedral Pt(IV) probes. It is our intention to report the synthesis and DNA-studies of $[Pt(phen)_3]^{4+}$ [phen = 1,10-phenanthroline]. Thus far, the synthesis of $[Pt(phen)_3]^{4+}$ has not been reported. The syntheses of $[PtCl_4(DIMP)]$ and $[PtCl_2(DIMP)_2][Cl]_2$ ($DIMP = 4,7$ -Dimethyl-1,10-phenanthroline) and $[Pt(en)(phen)_2][Fe(CN)_6]$ have been reported and characterized solely on microanalysis data (Power, 1975), (Kolobova,³ 1983). DNA-interactions with these complexes have not yet been reported.

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- 1 Author to whom correspondence regarding synthetic studies should be addressed. Present address: Department of Chemistry, Virginia Military Institute, Lexington VA, 24450.
 - 2 Present address: Department of Chemistry, Sweet Briar College, Sweet Briar VA, 24595.
 - 3 Present address: Department of Biology, Washington and Lee University, Lexington VA, 24450.
 - 4 Present address: Department of Chemistry, Sweet Briar College, Sweet Briar VA, 24595.
 - 5 Author to whom correspondence regarding crystallographic data should be addressed. Present address: Department of Chemistry, Purdue University, West Lafayette IN, 47907.

EXPERIMENTAL

We have recently begun the task of studying the chemistry of Pt(IV) complexes of phenanthroline and substituted derivatives of phenanthroline in an attempt to synthesize $[\text{Pt}(\text{phen})_3]^{4+}$ type compounds. Here we report the synthesis and characterization of the intermediate compound $[\text{Pt}(\text{phen})\text{Cl}_4]$ (1). Compound 1 (Figure 1) was prepared by refluxing 100 mg (0.21 mmol) of $\text{K}_2[\text{PtCl}_6]$ and a 5 fold excess of 1,10-phenanthroline in 50 mL of a 5M H_2SO_4 solution for 72 hours. After five hours, an orange precipitate formed on the walls of the reaction flask. After 72 hours, the orange solid was completely replaced by a yellow microcrystalline solid. The solid was collected on a sintered glass funnel and recrystallized from acetone and ether. Only a crude elemental analysis was obtained. Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{N}_2\text{PtCl}_4$: C 27.87, H 1.56, N 5.42, Cl 27.42 Pt 37.73 Found: C 28.01, H 1.79, N 5.23 Cl 26.22, Pt 38.1. Our experience has shown us that elemental micro-analysis of imene complexes of Iridium and Platinum often do not provide reliable data. This has been true even when the x-ray structure is exactly known and a pure crystalline sample is used for the micro analysis. Attempts to obtain further micro-analysis of (1) were not made. Crystals suitable for diffraction studies were obtained by slow diffusion from dimethylsulfoxide and ether. The crystals obtained were co-crystals of (1) and the solvent of crystallization (DMSO).

Gentle heating of a DMSO solution of 1 in the presence of AgNO_3 resulted in the precipitation of AgCl , presumably forming $[(\text{phen})\text{Pt}(\text{NO}_3)_4]$ (2). Combining a DMSO solution of (2) with a DMSO solution of excess phenanthroline resulted in the precipitation of a white solid (3) which we believe to be $[(\text{phen})_2\text{Pt}(\text{NO}_3)_2][\text{NO}_3]_2$. We are awaiting full characterization of (3) and will present these findings in a later publication.

Crystal Data: A single crystal of $\text{C}_{12}\text{H}_8\text{N}_2\text{PtCl}_4 \cdot \text{DMSO}$ was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range of $18 < \theta < 25^\circ$, measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are: $a = 10.285(3) \text{ \AA}$, $b = 10.767(1) \text{ \AA}$, $c = 16.516(3) \text{ \AA}$, $\beta = 91.47(2)^\circ$, $V = 1828(1) \text{ \AA}^3$. For $Z = 4$ and F.W. = 595.25, the calculated density is 2.16 g/cm³. The space group was determined to be $\text{P}2_1/\text{c}$. The data were collected at a temperature of $295 \pm 1 \text{ K}$ using the $\omega - 2\theta$ scan technique. The scan rate varied from 2 to 16°/min (in omega). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 52.6° . The scan range (in deg.) was determined as a function of θ to correct for the separation of the $\text{K}\alpha$ doublet (CAD4 Ops. Manual, 1977). Final R and R_w values were 0.041 and 0.053. The structure was solved using the Patterson heavy-atom method which revealed the position of the Pt atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\text{Sw} (|F_o| - |F_c|)^2$ and the weight w

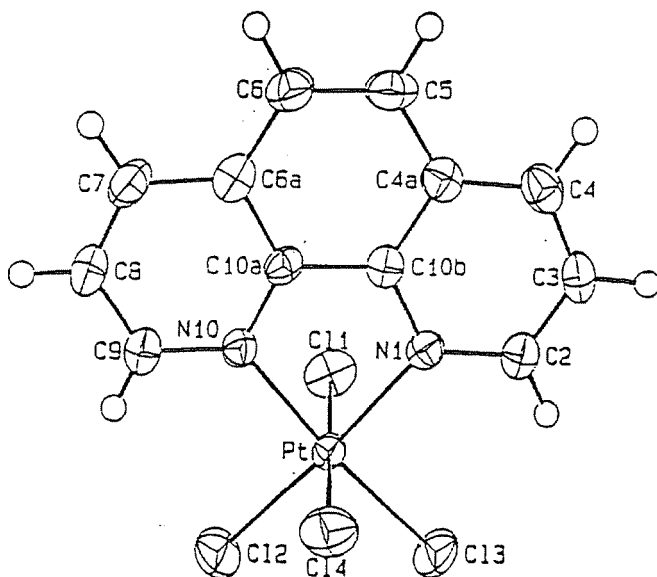


FIGURE 1. Molecular structure of $[\text{Pt}(\text{phen})\text{Cl}_4]$. Selected bond lengths and angles; N(1)-Pt 2.037 Å; N(10)-Pt 2.042 Å; Cl(1)-Pt 2.317 Å; Cl(2)-Pt 2.302 Å; Cl(3)-Pt 2.299 Å; Cl(4)-Pt 2.309 Å; N(1)-Pt-N(10) 80.6°; Cl(2)-Pt-Cl(3) 89.05°; Cl(2)-Pt-Cl(4) 91.6°; Cl(1)-Pt-Cl(2) 91.6°; Cl(1)-Pt-Cl(3) 90.93°; Cl(3)-Pt-Cl(4) 91.36°; N(1)-Pt-Cl(3) 95.1°; N(10)-Pt-Cl(2) 95.3°

is defined as per the Killian and Lawrence method with term of 0.020 and 1.0 (Killian & Lawrence, 1969). All calculations were performed on a VAX computer. Refinement was done using MolEN (Fair, 1990). Crystallographic drawings were done using programs ORTEP (Johnson, 1976) and/or PLUTON (Spek, 1991).

RESULTS AND DISCUSSION

The molecular structure of compound (1) is shown in Fig. 1, together with selected bond lengths and angles. Several features of the structure are noteworthy. The N-Pt-N bond angle is severely distorted from the anticipated 90° for an octahedral geometry to 80.6°. The N-Pt bond lengths are 2.037 Å and 2.042 Å. These values are similar to those seen in other metal-coordinated phenanthroline complexes (Goldstein, Barton & Berman, 1986), (Anderson, 1973), (Zalkin, Templeton & Ueki, 1973), (Gould, Stephenson & Thomson, 1980), (Bonneson, Walsh, Pennington, Cordes & Durham, 1983). For example, the average N-Ru-N bond angle in tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) $[\text{Ru}(\text{DIPP})_3]^{2+}$ is 79.7°, and the average N-Ru bond length found in $[\text{Ru}(\text{DIPP})_3]^{2+}$ is 2.06 Å (Goldstein, Barton & Berman, 1986). It is also interesting to note that the Cl-Pt-Cl bond angles of compound 1 (91.6°, 90.9°, 89.1°, 91.6°) are not significantly distorted from a purely octahedral orientation. Furthermore, there seems to be little steric repulsion between the α -hydrogens on phenanthroline and the chlorides in the equatorial plane as indicated by the N-Pt-Cl bond angles of 95.1° and 95.3°. These data tend to indicate that the synthesis of $[\text{Pt}(\text{phen})_3]^{4+}$ will not be inhibited by any intrinsic steric barrier. We feel that the absence of

$[\text{Pt}(\text{phen})_3]^{4+}$ in the published literature is a result of the difficulties of solvating a 4+ cation. In our studies of Pt(IV)-phenanthroline complexes, we have encountered numerous insoluble precipitates. Current synthetic studies involve the use of alternative counter anions in an attempt to produce a soluble salt of $[\text{Pt}(\text{phen})_3]^{4+}$.

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LITERATURE CITED

- Anderson, O. P. 1973. Crystal and Molecular Structure of tris-(1,10-phenanthroline)copper(II)perchlorate. *J. Am. Chem. Soc., Dalton Trans.*, 1237-1241.
- Barton, J. K. 1989. Targeting DNA Sites with Chiral Metal Complexes. *Pure and Appl. Chem.* 61: 563-564.
- Barton J. K. 1986. Metals and DNA: Molecular Left-Handed Complements. *Science* 233: 727-734.
- Bonneson, P., J.L. Walsh, W.T. Pennington, A.T. Cordes, B. Durham. 1983. Six Coordinate Complexes with 1,10-phenanthroline ligands in the Trans Configuration. Preparation of Trans-bis (1,10-phenanthroline) ruthenium (II) Complexes and Crystal Structure of Trans-bis (1,10-phenanthroline) bis (pyridine) ruthenium(II) hexafluorophosphate. *Inorg. Chem.* 22(12): 1761-1765.
- CAD4 Operations Manual. 1977. Enraf-Nonius, Delft.
- Fair, C. K. 1990. MolEN Structure Determination System, Delft Instruments, Delft, The Netherlands.
- Fleisher, M. B., K.C. Waterman, N.J. Turro, J.K. Barton. 1986. Light-Induced Cleavage of DNA by Metal Complexes. *Inorg. Chem.* 25: 3549-3551.
- Goldstein, B. M., J.K. Barton, H.M. Berman. 1986. Crystal and Molecular Structure of a Chiral-Specific DNA-Binding Agent: Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II). *Inorg. Chem.* 25: 842-847.
- Gould, R. O., Stephenson, T. A., Thomson, M. A. 1980. Metal Complexes of Sulfur Ligands: Part 20. Reactions of bis(dimethylphenylphosphine)bis(monochlorobenzoato)ruthenium(II) with some bidentate nitrogen-donor Lewis Bases and X-ray structural analysis of two isomers of bis(dimethylphenylphosphine)bis(monochlorobenzoato)(1,10-phenanthroline)ruthenium(II). *J. Am. Chem. Soc., Dalton Trans.*, 804-809.
- Johnson, C. K. 1976. ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, US.
- Killean R. C. G. J.L. Lawrence. 1969. Least-Squares Weighting Schemes for Diffractometer-Collected Data. IV. Effect of Random Errors in the Form Factors Resulting from Bonding. *Acta Crystallogr., Sect. B*, 25: 1750.
- Kolobova, L. N., A.K. Pyartman, L.A. Obozova, V.E. Mironov. 1983. *Zhurnal Neorganicheskoi Khimii.* 22(2): 189-191.

- Mack, D. P., P.B. Dervan. 1990. Nickel-Mediated Sequence-Specific Oxidative Cleavage of DNA by a Designed Metallo Protein. *J. Am. Chem. Soc.* 112: 4604-4606.
- Pope, L. E., D.S. Sigman. 1984. Secondary Structure Specificity of the Nuclease Activity of the 1,10-phenanthroline-copper complex. *Proc. Natl. Acad. Sci. USA* 81: 3-7.
- Power, L. F. 1975. Platinum (IV) and Palladium (IV) complexes of 2,9-dimethyl-1,10-phenanthroline. *Syn. React. Inorg. Metal. Org. Chem.*, 5(3):181-187.
- Pyle, A. M., E.C. Long, J.K. Barton. 1989. Shape-Selective Targeting of DNA by (Phenanthrenequinone diimine)rhodium(III) Photocleaving Agents. *J. Am. Chem. Soc.* 111: 4520-4522.
- Spek, A. L. 1991. PLUTON. Molecular Graphics Program. Univ. of Utrecht, The Netherlands
- Zalkin, A., D.H. Templeton, T. Ueki. 1973. Crystal Structure of I-tris-(1,10-phenanthroline iron(II) (antimony(III) d-tartrate)-octahydrate. *Inorg. Chem.*, 12(7): 1641-1646.

