# Electronic Supporting Infirmation

# The first example of metallocene-like coordination mode of fully deprotonated 2,3,5,6-tetrahydroxy-1,4-benzoquinone (THBQ$^{4-}$): A mixed-valence heptanucler palladium complex [Pd$_7$(THBQ)$_2$(tben)$_6$](PF$_6$)$_4$ (tben = *N,N,N',N'*-tetrabenzylethylenediamine)

**Eiji Asato, Ayano Kyan, Tomokura Madanbashi, Toshihide Tamura, Makoto Tadokoro and Motohiro Mizuno**

1)      **X-ray structure report**

2)      **$^1$H NMR spectrum of complex 1 measured in deuterated DMF**

# 1)    X-ray structure report

*Experimental*

## Data Collection

A black prism crystal of $C_{198}H_{201}F_{24}N_{15}O_{12}P_4Pd_7$ having approximate dimensions of 0.38 x 0.35 x 0.31 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-K$\alpha$ radiation.

Indexing was performed from 0 images that were exposed for 0 seconds. The crystal-to-detector distance was 55.17 mm.

Cell constants and an orientation matrix for data collection corresponded to a R-centered trigonal cell (laue class: -3) with dimensions:

$$a = 19.3100(7) \text{ Å}$$
$$c = 40.620(2) \text{ Å}$$
$$V = 13117.0(10) \text{ Å}^3$$

For Z = 3 and F.W. = 4307.52, the calculated density is 1.636 g/cm$^3$. Based on the systematic absences of:

hkil:   -h+k+l $\pm$ 3n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

R-3 (#148)

The data were collected at a temperature of -100 $\pm$ 1$^O$C to a maximum 2$\theta$ value of 54.9$^O$. A total of 1400 oscillation images were collected. A sweep of data was done using $\phi$ scans from -80.0 to 100.0$^O$ in 0.3$^O$ step, at $\omega$=0.0$^O$ and $\chi$ = 0.0$^O$. The exposure rate was 33.3 [sec./$^O$]. The detector swing angle was 24.97$^O$.  A second sweep was performed using $\omega$ scans from -15.0 to 45.0$^O$ in 0.3$^O$ step, at $\chi$=90.0$^O$ and $\phi$ = 0.0$^O$. The exposure rate was 33.3 [sec./$^O$]. The detector swing angle was 24.97$^O$.   Another sweep

was performed using $\omega$ scans from -15.0 to 45.0$^O$ in 0.3$^O$ step, at $\chi$=90.0$^O$ and $\phi$ = 90.0$^O$. The exposure rate was 33.3 [sec./$^O$]. The detector swing angle was 24.97$^O$. Another sweep was performed using $\omega$ scans from -15.0 to 45.0$^O$ in 0.3$^O$ step, at $\chi$=90.0$^O$ and $\phi$ = 180.0$^O$. The exposure rate was 33.3 [sec./$^O$]. The detector swing angle was 24.97$^O$. Another sweep was performed using $\omega$ scans from -15.0 to 45.0$^O$ in 0.3$^O$ step, at $\chi$=90.0$^O$ and $\phi$ = 270.0$^O$. The exposure rate was 33.3 [sec./$^O$]. The detector swing angle was 24.97$^O$. The crystal-to-detector distance was 55.17 mm. Readout was performed in the 0.273 mm pixel mode.

## Data Reduction

Of the 32304 reflections that were collected, 6609 were unique ($R_{int}$ = 0.037); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows:

$$F^2 = [\Sigma(P_i - mB_{ave})] \cdot \; Lp^{-1}$$

where $P_i$ is the value in counts of the i$^{th}$ pixel
m is the number of pixels in the integration area
$B_{ave}$ is the background average
Lp is the Lorentz and polarization factor

$$B_{ave} = \Sigma(B_j)/n$$

where n is the number of pixels in the background area
$B_j$ is the value of the j$^{th}$ pixel in counts

$$\sigma^2(F^2_{hkl}) = [(\Sigma P_i) + m((\Sigma(B_{ave} - B_j)^2)/(n\text{-}1))] \cdot \; Lp \cdot \; errmul + (\; erradd \cdot \; F^2)^2$$

where erradd = 0.00
errmul = 1.00

The linear absorption coefficient, $\mu$, for Mo-K$\alpha$ radiation is 8.349 cm$^{-1}$. A numerical absorption correction was applied which resulted in transmission factors ranging from 0.727 to 0.772. The data were corrected for Lorentz and polarization effects.

## Structure Solution and Refinement

The structure was solved by heavy-atom Patterson methods[2] and expanded

using Fourier techniques[3]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[4] on $F^2$ was based on 6609 observed reflections and 389 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| / \Sigma \, |Fo| = 0.0478$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \Sigma \, w(Fo^2)^2]^{1/2} = 0.1091$$

The standard deviation of an observation of unit weight[5] was 1.11. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.43 and -1.00 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL-97[11].

SPECIAL DETAILS OF THE REFINEMENT

One phenyl ring including C16 is separated into two components, thus treated as being disordering. The disorder and its occupancy are refined. Two PF6 anions are also treated as a disorder model. Since the P1, F1, and F2 are located on the three-fold axis, F3--F6 are treated with the occupation of 1/3. The other PF6 anion exhibited strong disorder, and separated into three components present on the three-fold axis. The occupancy of each PF2 part as the asymmetric unit was also refined, and converged to 0.456, 0.298 and 0.248 (= total 1.00). At the final stage of refinement, any reasonable peaks for acetonitrile molecules expected from the elemental analysis were not found. A possible reason should be strong disorder or low occupancy of the molecules. Based on the assumption that the acetonitrile is disordering, the solvent molecules were included in crystal's formula and SQEESE program in PLATON[12] was used to refine the structure at the final refinement process.

*References*

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) PATTY: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., Garcia-Granda, S., Gould, R.O., Smits, J.M.M. and Smykalla, C. (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o{}^2 - F_c{}^2)^2 \qquad \text{where w = Least Squares weights.}$$

(5) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_o - N_v)]^{1/2}$$

where: $N_o$ = number of observations
$N_v$ = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(11) SHELX97: Sheldrick, G.M. (1997).

(12) PLATON (Speck, 2003). Speck, A.L. (2003). J. Appl. Cryst. 36, 7-13.

## EXPERIMENTAL DETAILS

### A. Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{198}H_{201}F_{24}N_{15}O_{12}P_4Pd_7$ |
| Formula Weight | 4307.52 |
| Crystal Color, Habit | black, prism |
| Crystal Dimensions | 0.38 X 0.35 X 0.31 mm |
| Crystal System | trigonal |
| Lattice Type | R-centered |
| Detector Position | 55.17 mm |
| Pixel Size | 0.137 mm |
| Lattice Parameters | $a = 19.3100(7)$ Å <br> $c = 40.620(2)$ Å <br> $V = 13117.0(10)$ Å$^3$ |
| Space Group | R-3 (#148) |
| Z value | 3 |
| $D_{calc}$ | 1.636 g/cm$^3$ |
| $F_{000}$ | 6564.00 |
| $\mu(MoK\alpha)$ | 8.349 cm$^{-1}$ |

## B. Intensity Measurements

| | |
|---|---|
| Detector | Rigaku Mercury |
| Goniometer | Rigaku AFC7 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71070 Å) graphite monochromated |
| Detector Aperture | 70 mm x 70 mm |
| Data Images | 1400 exposures |
| $\phi$ oscillation Range ($\omega$=0.0, $\chi$=0.0) | -80.0 - 100.0$^{O}$ |
| Exposure Rate | 33.3 sec./$^{O}$ |
| Detector Swing Angle | 24.97$^{O}$ |
| $\omega$ oscillation Range ($\chi$=90.0, $\phi$=0.0) | -15.0 - 45.0$^{O}$ |
| Exposure Rate | 33.3 sec./$^{O}$ |
| Detector Swing Angle | 24.97$^{O}$ |
| $\omega$ oscillation Range ($\chi$=90.0, $\phi$=90.0) | -15.0 - 45.0$^{O}$ |
| Exposure Rate | 33.3 sec./$^{O}$ |
| Detector Swing Angle | 24.97$^{O}$ |
| $\omega$ oscillation Range ($\chi$=90.0, $\phi$=180.0) | -15.0 - 45.0$^{O}$ |
| Exposure Rate | 33.3 sec./$^{O}$ |
| Detector Swing Angle | 24.97$^{O}$ |
| $\omega$ oscillation Range ($\chi$=90.0, $\phi$=270.0) | -15.0 - 45.0$^{O}$ |
| Exposure Rate | 33.3 sec./$^{O}$ |

| | |
|---|---|
| Detector Swing Angle | 24.97$^o$ |
| Detector Position | 55.17 mm |
| Pixel Size | 0.137 mm |
| $2\theta_{max}$ | 54.9$^o$ |
| No. of Reflections Measured | Total: 32304<br>Unique: 6609 ($R_{int}$ = 0.037) |
| Corrections | Lorentz-polarization<br> Absorption<br> (trans. factors: 0.727 - 0.772)<br> Decay (0.00% increase) |

## C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Patterson Methods (DIRDIF99 PATTY) |
| Refinement | Full-matrix least-squares on $F^2$ |
| Function Minimized | $\Sigma\, w\, (Fo^2 - Fc^2)^2$ |
| Least Squares Weights | $w = 1/\,[\ \sigma^2(Fo^2) + (0.0422 \cdot P)^2$ $+\ 120.7983 \cdot \quad P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$ |
| $2\theta_{max}$ cutoff | $54.9^o$ |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (All reflections) | 6609 |
| No. Variables | 389 |
| Reflection/Parameter Ratio | 16.99 |
| Residuals: R1 (I>2.00$\sigma$(I)) | 0.0478 |
| Residuals: R (All reflections) | 0.0514 |
| Residuals: wR2 (All reflections) | 0.1091 |
| Goodness of Fit Indicator | 1.111 |
| Max Shift/Error in Final Cycle | 0.001 |
| Maximum peak in Final Diff. Map | 1.43 e$^-$/Å$^3$ |
| Minimum peak in Final Diff. Map | -1.00 e$^-$/Å$^3$ |

**2)** $^1$**H NMR spectrum of complex 1 measured in deuterated DMF**