

The Refinement of the Crystal Structure of Norbornadiene Palladium Chloride

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The crystal structure of norbornadiene palladium chloride has been refined with data obtained by counter methods from crystals maintained at liquid nitrogen temperature. After refinement the conventional discrepancy index $R=0.0275$. The carbon-carbon single bond distances in the norbornadiene molecule are normal: 1.547, 1.552, 1.554 (± 0.006) Å; the double bond distances are barely significantly longer than normal: 1.366, 1.366 (± 0.010) Å. The observed double bond distance is now compatible with the infrared spectrum of the complexed olefin.

Introduction

In the original structure determination of norbornadiene palladium chloride (Baenziger, Doyle & Carpenter, 1961) the bond distances in the olefin were found to be abnormally long. The errors were also large, so that these distances were not to be taken too seriously. In an effort to obtain more reliable values, intensity measurements were repeated at room temperature, this second time with a proportional counter instead of by visual estimation from films (Baenziger, Doyle, Richards & Carpenter, 1961). The limits of error in this determination were smaller and the bond distances were also shortened to the extent that the C-C single bonds in the olefin could be considered normal. The two C=C double bond distances were 1.46 Å. The standard deviation of 0.037 Å in these distances meant that the double bond distances were just barely significantly longer than 1.34 Å, the normal double bond distance.

The diffraction intensities of norbornadiene palladium(II) chloride have once again been remeasured, this time at the temperature of liquid nitrogen, with a proportional counter and a modified Weissenberg apparatus (Evans, 1953). The cooling system, by the inherent nature of its design, maintained the crystal at a constant temperature not detectably different (by Cu-constantan thermocouple) from that of liquid nitrogen (Richards, 1964).

Experimental

Two crystals were used to obtain the data. Crystal I, a cylinder, 0.045×0.250 mm ($\mu R=0.57$), was used to obtain layers zero through five about the b axis. Crystal II, a cube ($\mu R=0.60$), was used to obtain data about the a axis from layers zero through six which had not already been obtained from crystal I. No overlap in reflection measurements was made. All equivalent reflections within a layer were measured, the average deviation in intensity being 2%. The intensity of a reference reflection within each layer was reproduced to 2.5% on the average. Several low angle reflections were

not measured because of their extremely high intensity; all measured reflections were utilized in the refinement. All data were corrected for absorption effects (cylinder assumed for crystal I, sphere assumed for crystal II) and Lorentz and polarization factors. A total of 838 independent reflections were measured. Nickel filtered Cu K radiation and a pulse height analyzer were used in conjunction with the proportional counter.

Norbornadiene palladium(II) chloride is orthorhombic; the space group is $Pnma$. The unit-cell dimensions at liquid nitrogen temperature are $a=9.316 \pm 0.0015$, $b=7.085 \pm 0.001$, $c=11.685 \pm 0.0015$ Å. The cell dimensions were obtained from back-reflection Weissenberg films with the use of an analytical least-squares extrapolation method to minimize systematic errors.

Refinement of the data

A full-matrix least-squares program written for the IBM 7040 computer was used which permitted intermixing of individual anisotropic and isotropic temperature factors and refining on any number of scale parameters, and provided for both real and imaginary dispersion corrections for any atom. The program minimizes $\sum w(F^2_{\text{obs}} - F^2_{\text{calc}})^2$. The refinement included anisotropic temperature factors for all atoms except hydrogen, hydrogen atoms being given a fixed B value of 1.0 Å² (average value of B for carbon atoms); the complete (both real and imaginary parts) dispersion correction to the atom scattering factors for palladium and chlorine atoms; and one overall scale parameter. The uncorrected scattering factors were obtained by interpolation of the values listed in *International Tables for X-ray Crystallography* (1962) for Pd, Cl, C and H. Hydrogen positions were allowed to vary. Inclusion of an extinction correction produced no significant changes either in agreement or in positional parameters. Refinement with one overall scale parameter gave a slightly higher R value (0.0275) and slightly different thermal parameters but not significantly different positional parameters than the refinement with scale parameters for each group of data ($R=0.0266$). Refinements were continued until changes in the parameters

Table 1. Atom parameters from the low temperature counter data

	$s(x)$	$s(y)$	$s(z)$	B_{11} $s(B_{11})$	B_{22} $s(B_{22})$	B_{33} $s(B_{33})$ $\times 10^5$	B_{12} $s(B_{12})$	B_{13} $s(B_{13})$	B_{23} $s(B_{23})$
Pd	0.60144 0.00004	0.25000	0.47763 0.00004	191 4	427 11	132 3		-24 6	
Cl(1)	0.53180 0.00015	0.25000	0.28674 0.00011	393 14	520 39	170 8		-70 18	
Cl(2)	0.36886 0.00012	0.25000	0.54600 0.00012	225 13	560 36	269 10		25 16	
C(1,4)	0.84450 0.00044	0.41036 0.00065	0.57929 0.00033	327 34	273 100	218 26	-340 113	-8 17	-328 83
C(2,3)	0.70051 0.00041	0.34646 0.00068	0.63414 0.00030	331 36	694 121	132 24	48 120	-27 49	-184 87
C(5,6)	0.82012 0.00036	0.34644 0.00072	0.45379 0.00032	211 35	631 118	198 26	-126 104	51 49	10 86
C(7)	0.94333 0.00063	0.25000	0.62247 0.00052	324 58	623 170	237 39		-15 75	
H(1,4)	0.8692 0.0054	0.5358 0.0092	0.5944 0.0054	1.00 Å ² 1.36					
H(2,3)	0.6367 0.0050	0.4413 0.0085	0.6701 0.0051	1.00					
H(5,6)	0.8156 0.0058	0.4320 0.0083	0.3906 0.0050	1.00					
H(7)	0.0589 0.0085	0.2500	0.5791 0.0076	1.00					
H(7')	0.9473 0.0086	0.2500	0.7106 0.0069	1.00					

were less than 1×10^{-5} . The parameters listed in Table 1 correspond to the refinement with one overall scale parameter.

Since hydrogen atoms had not been included in previous calculations of structures of this type, one set of refinements was made in which the H atoms were omitted. A minimum R value of 0.0343 was obtained, and the carbon atom parameters had shifted so that the C-C distances were 1.570, 1.564 and 1.558 Å; the C=C distances were 1.384 and 1.390 Å. The Pd and Cl parameters did not change significantly. Thus, omission of H atoms from the previous calculations could give rise to an appreciable systematic error.

Discussion

The carbon-carbon single-bond distances obtained in this refinement are very nearly identical, with only slightly more than one standard deviation separating the longest from the shortest distance. If the three bond lengths are considered as a group, the T^2 test of Cruickshank & Robertson (1953) gives a value of 14.3, so that three bond lengths are not longer than 1.54 Å at the 0.1% level of significance. If the double-bond distances are considered in the same manner, the value of T^2 is 15. Thus, although the double bonds individually are not significantly longer than the double bond in ethylene (1.339 Å), the pair of independent double bonds are significantly longer, the 0.1% level of significance being used in both cases. The observed bond length, 1.366 Å, is in conformity with the change in the infrared spectrum, since a change of 140 cm^{-1} in the double bond stretching frequency could reasonably correspond to a change of 0.03 Å.

The palladium-chlorine distances are unequal by a significant amount, since the difference in bond distances, 0.013 Å, is almost ten times the standard deviation. This difference is undoubtedly connected with the packing arrangement in the solid and the unequal change in cell dimensions on cooling the crystal. The

Table 2. Bond distances from this refinement and a comparison of the dimensions of free norbornadiene with those of norbornadiene in norbornadiene palladium (II) chloride

	Average	From electron diffraction*
Pd-Cl(1)	2.323 ± 0.0014 Å	
Pd-Cl(2)	2.310 ± 0.0013	
Pd-C(1,2)	2.159 ± 0.0037	
Pd-C(5,6)	2.166 ± 0.0036	
H-C(1,4)	0.94 ± 0.06	
H-C(2,3)	0.98 ± 0.06	
H-C(5,6)	0.95 ± 0.06	
H-C(7)	1.18 ± 0.08	
	1.03 ± 0.08	
C(1)-C(2)	1.554 ± 0.0056	1.553
C(1)-C(6)	1.552 ± 0.0057	
C(1)-C(7)	1.547 ± 0.0059	1.547
C(2)-C(3)	1.366 ± 0.0096	1.366
C(5)-C(6)	1.366 ± 0.010	
C(2)-C(6)	2.383	2.369
C(6)-C(7)	2.380	2.374
C(2)-C(7)	2.367	
C(2)-C(5)	2.747	2.718
C(1)-C(5)	2.348	2.349
C(1)-C(3)	2.350	
C(1)-C(2)-C(3)	106.9° ± 0.4°	107.0°
C(4)-C(5)-C(6)	107.0 ± 0.4	109.1°
C(2)-C(1)-C(7)	99.5 ± 0.4	100.0
C(6)-C(1)-C(7)	100.4 ± 0.4	96.4
C(2)-C(1)-C(6)	100.3 ± 0.3	100.3
		102.2

* Data of V. Schomaker from Wilcox, Winstein & McMillan (1960).

difference, though significant, is, nevertheless, small, and does not correspond to more than a few calories per mole in the Pd-Cl bond energy.

The bond distances and angles of the norbornadiene molecule are compared with those reported for the free olefin obtained from an electron diffraction study by Schomaker (Wilcox, Winstein & McMillan, 1960) in Table 2. Some additional distances are given to indicate the degree of regularity in the structure. Since the reliability of the electron diffraction data is unknown, significant statements cannot be made about the agreement of the values. Using either the electron diffraction values or the values of 1.54 and 1.34 Å for single and double bonds as criteria of normalcy, it is evident that very little change in the olefin occurs on forming the complex. The double bonds which are coordinated are probably lengthened a small amount. The infrared spectrum, except for the uncertainty of

interpretation, appears to give a more sensitive indication of changes in the olefin.

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Accuracy of an Automatic Diffractometer. Measurement of the Sodium Chloride Structure Factors

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The sodium chloride structure factors have been measured with the automatic diffractometer, PEXRAD. Five different single-crystal spheres were used, with various experimental measurement techniques. Analysis of the error in the measurements has shown the average structure factor (F_{meas}) for the best techniques to have a standard error of 3.5 to 4.0% $|F_{\text{meas}}|$. About half this error is due to instrumental causes. The remainder is produced by error in the absorption coefficients, crystal size determination, extinction coefficients *etc.* The mean values of the Debye-Waller factors are $B(\text{Na}) = 1.639 \pm 0.037$, $B(\text{Cl}) = 1.326 \pm 0.023 \text{ \AA}^2$, corresponding to a characteristic temperature $\theta = 287 \text{ }^\circ\text{K}$, in good agreement with the θ derived from specific heat and from elastic constant measurements. It is shown that low R values do not necessarily indicate the absence of systematic error.

Introduction

Automatic diffractometers are composed of two separate, intimately connected, systems. These are colloquially referred to as the *hardware* and *software* systems. By hardware is meant the assembly of mechanical, electronic and similar components; by software, the control and processing programs. A description of the hardware and software systems alone, while necessary for understanding the operation of an automatic diffractometer, is incomplete without a measure of the accuracy of the whole system. A subsidiary, although important, aspect of this total description includes the rate at which data are measured, and also the amount of personal time required in running the diffractometer.

In the case of one automatic diffractometer, PEXRAD*, both the hardware (Abrahams, 1962) and the software (Cetlin & Abrahams, 1963) systems have been described. In addition, an analysis has been made of the various sources of error common to all automatic diffractometer systems, and criteria have been presented (Abrahams, 1964a) for their detection. The present paper uses these criteria to assess the accuracy of PEXRAD under normal operating conditions. The best values obtained in this study for the Debye-Waller factors for the sodium and chlorine atoms in rocksalt are given. Typical times for measurement of structure factors, and the personal time involved in these measurements are also presented.

* Programmed Electronic X-ray Automatic Diffractometer.