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A Neutron Diffraction Study of the Crystal Structure of Deuterated Ammonium Tetrachloropalladate(II) at Low and Ambient Temperatures

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The crystal structure of deuterated ammonium tetrachloropalladate at 125 and 295 K has been studied by neutron diffraction analysis. The results confirm the previously reported X-ray structure; at both temperatures the structure is best described in the tetragonal space group *P4/mmm*. Lattice parameters are $a=b=7.20(1)$ Å, $c=4.21(1)$ Å at 125 K and $a=b=7.22(1)$ Å, $c=4.24(1)$ Å at 295 K. $Z=1$. Full matrix least squares refinements on F^2 converged at $R(F^2,125\text{ K})=5.2$ % and $R(F^2,295\text{ K})=7.7$ %. The $[PdCl_4]^{2-}$ ions are square planar with Pd—Cl bond lengths of 2.314(4) Å. Deuterium atoms are at both temperatures disordered, corresponding to two equally probable orientations of the ammonium ion with two identical sets of hydrogen bonds N—D···Cl; *i.e.* the ammonium ions in $(ND_4)_2[PdCl_4]$ are not freely rotating neither at 125 nor at 295 K. The possibilities of structural distortions at low temperature, as suggested by Adams and Berg from interpretation of low-temperature far infrared spectra, were not substantiated by refinement in space groups less symmetric than *P4/mmm*. It is concluded that if such distortions do occur they must be highly time or space dependent not to appear in the diffraction experiment.

The structural chemistry of palladium(II) and platinum(II) is dominated by the square planar coordination and very few exceptions with minor distortions are known. It was recently suggested by Adams and Berg [1] that $(NH_4)_2[PdCl_4]$ should be one such exception according to their interpretation of the low-temperature far infrared spectra of $A_2[PdCl_4]$ and $A_2[PtCl_4]$ with $A=K$, NH_4 or ND_4. They had difficulties in interpreting the spectra on the basis of the known room temperature structures.[2–4] Adams and Berg derived several kinds of lattice distortions which might occur at low temperatures and which might explain the spectra. Since the most pronounced spectral changes on cooling were found in $(NH_4)_2[PdCl_4]$, we felt it of interest to investigate the room and low-temperature crystal structure of $(ND_4)_2[PdCl_4]$.

EXPERIMENTAL

Crystals of $(ND_4)_2[PdCl_4]$ were obtained by repeated re-crystallization of $(NH_4)_2[PdCl_4]$ [1] in heavy water in a desiccator over dry silica gel. The single crystal used for data collection had a volume of 7.2 mm^3 ($a\times b\times c\simeq 1.6\times 0.9\times 5.0$ mm) and was mounted on a Hilger-Ferranti four-circle diffractometer at the Danish Atomic Energy Commission Research Establishment, Risø. The (002) reflection from a Be monochromator crystal provided an incident neutron beam of wavelength 1.070 Å. Data collection was carried out at low temperature, 125 K, achieved in a stream of cold nitrogen gas [5] and at ambient temperature, 295 K. A neutron structure factor calculation based upon the previously determined X-ray structure [2,3] was used to select expected stronger reflections for data collection. Bragg intensities were measured with a BF_3 detector using ω-step scan technique. The intensities were integrated in steps of 0.04° over a scan width $u=2.0°$ tg $\theta+2.4°$. A total of 264 reflections at 125 K and 317 reflections at 295 K were collected within a maximum value of $\sin\theta/\lambda=0.855$. The integrated intensities were evaluated by a method [6] which divides the step-scanned profile into peak and background in such a way that $\sigma_{count}(I)/I$ is minimized, where I is the

integrated intensity and $\sigma_{count}(I)$ its estimated standard deviation based on counting statistics. Two standard reflections (040) and (002) were measured for every 18 reflections and showed an increase in intensity amounting to 1 % over the data collection period both at low and room temperatures. Intensities were corrected for this long term trend and were also corrected for absorption, at first using the linear absorption coefficient $\mu = 0.504$ cm^{-1} calculated for $(ND_4)_2[PdCl_4]$ from tabulated mass absorption coefficients and incoherent scattering cross sections,[7] but later recalculated to $\mu = 0.801$ cm^{-1}, when it became evident that deuteration was only partial. The incoherent scattering cross section for the hydrogen nucleus was given the value of 40 barn. The intensities were reduced to squared structure factors, $F_{hkl,\,obs}^2$ by application of the inverse Lorentz factor, $\sin 2\theta_{hkl}$. Symmetry related reflections and remeasurements were averaged giving 163 and 169 unrelated structure factors in the low temperature and room temperature data set, respectively. The corresponding internal agreement factors, $R_{int}(F_{obs}^2) = \sum|F_{obs}^2 - \langle F_{obs}^2\rangle|/\sum F_{obs}^2$ were 0.036 and 0.014. In the refinements scattering lengths for Cl and N were those of the Neutron Diffraction Commission,[8] while for Pd and D they were included as parameters. The resulting values, b(Pd, 125 K) = 0.51(2) × 10^{-12} cm and b(Pd, 295 K) = 0.51(3) × 10^{-12} cm are just significantly different from the tabulated [8] value of 0.60 × 10^{-12} cm. For deuterium, b(D, 125 K) = 0.466(7) × 10^{-12} cm and b(D, 295 K) = 0.428(12) × 10^{-12} cm is interpreted as due to partial deuteration of the sample crystal. The degree of deuteration is calculated to a value of 79(1) % using b(D) = 0.6672 × 10^{-12} cm and b(H) = −0.374 × 10^{-12} cm.[8]

X-Ray film exposures of a crystal cooled by a cryotip mounted on a precession camera indicated no phase changes as low as 90 K, and no doubling of the tetragonal a axis was observed.

CRYSTAL DATA

$(ND_4)_2[PdCl_4]$. M.W. = 292.34 g/mol. Tetragonal. Space group $P4/mmm$ (D_{4h}^1, No. 123). $a = b = 7.20(1)$ Å and $c = 4.21(1)$ Å at 125 K, and $a = b = 7.22(1)$ Å and $c = 4.24(1)$ Å at 295 K. V(125 K) = 218.25 Å^3. V(295 K) = 221.02 Å^3. $Z = 1$. D_c (295 K) = 2.196 g/cm^3, $D_o = 2.1$ g/cm^3 (for the hydrogen compound).[3]

RESULTS AND DISCUSSION

The structure of the compound $(NH_4)_2[PdCl_4]$ was previously [2,3] solved by means of X-ray film data and refined in space group $P4/mmm$ to give Pd in position a (0,0,0); N in e (0,½,½) and Cl in j (x,x,0) with $x \simeq 0.23$.

A difference Fourier map based on the observed neutron structure factors and those calculated from the above structural information showed – for both temperatures – just one predominant peak in the asymmetric unit. The peak is at a general position almost on the line of connection between N and Cl, with distances ~1.00 Å from N and ~2.32 Å from Cl. The peak is therefore suitable for accomodation of D, but the 16-fold degeneracy of the general position infers fractional occupation (disorder).

Full matrix least-squares refinement of the structure was carried to convergence in space

Table 1. Atomic coordinates expressed as fraction of the cell edges and thermal parameters in Å^2 × 10^3. Estimated standard deviations in units of least significant digit are given in parentheses. The temperature factor is of the form exp $[-2\pi^2(\sum_i\sum_j h_i h_j a_i^* a_j^* U_{ij})]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
125 K; $R(F^2) = \sum\|F_o^2 - k\|F_c^2\|\|/\sum F_o^2 = 5.2$ % (k = scaling multiplier)									
Pd	0.0000	0.0000	0.0000	18(5)	18	15(3)	0	0	0
Cl	0.2266(3)	0.2266	0.0000	25(1)	25	35(1)	−1(1)	0	0
N	0.0000	0.5000	0.5000	36(2)	26(1)	30(1)	0	0	0
D	0.0811(7)	0.4194(6)	0.3581(7)	55(3)	41(2)	45(2)	11(1)	12(2)	−10(2)
295 K; $R(F^2) = 7.7$ %									
Pd	0.0000	0.0000	0.0000	25(9)	25	26(6)	0	0	0
Cl	0.2266(5)	0.2266	0.0000	34(2)	34	50(2)	−6(1)	0	0
N	0.0000	0.5000	0.5000	57(3)	33(2)	35(2)	0	0	0
D	0.0770(15)	0.4231(14)	0.3601(12)	82(8)	60(6)	69(3)	15(2)	18(5)	−11(4)

Table 2. Distances (Å) and angles (°) for $(ND_4)_2[PdCl_4]$ as refined in space group *P4/mmm*. Distances corrected for riding thermal motion are quoted in italics.

	125 K	295 K
Pd – Cl	2.307(5)	2.307(7)
	2.313(5)	*2.315(7)*
N – D	1.017(4)	0.980(8)
	1.044(4)	*1.023(9)*
D – Cl	2.302(5)	2.337(8)
N – Cl	3.312(4)	3.312(4)
Cl – Pd – Cl	90.00	90.00
D – N – D	108.1(4)	106.1(9)
N – D – Cl	171.9(4)	173.0(1.0)

group *P4/mmm* as well as in the less symmetric space groups suggested by Adams and Berg.[1] A scale factor, an isotropic extinction parameter,[9] positional and anisotropic thermal parameters were refined by minimizing the expression $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F^2)$. For both the low and the room temperature data set there was no significant improvement of fit by lowering the $P4/mmm$-D_{4h}^1 symmetry and no significant change of atomic positional parameters for nonhydrogen atoms, which means that in all space groups and at both temperatures the $[PdCl_4]$ configuration appears planar within the experimental uncertainty. Final parameters and agreement factors are given in Table 1 and bonded distances and angles in Table 2. A list of structure factors can be obtained upon request. Extinction corrections exceeded 10 % for only two reflections.

The molecular packing and the atomic thermal motion at 125 and 295 K is depicted in Fig. 1 as two stereo pairs of drawings. It is conceivable that the libration of the ammonium ions especially at 295 K are so great that the harmonic approximation applied in the description of the thermal motion is invalidated, which may explain the poorer agreement factor for the presumably better 295 K data set.

The square planar chlorine configuration around Pd makes disorder very plausible. The disorder model of space group *P4/mmm*

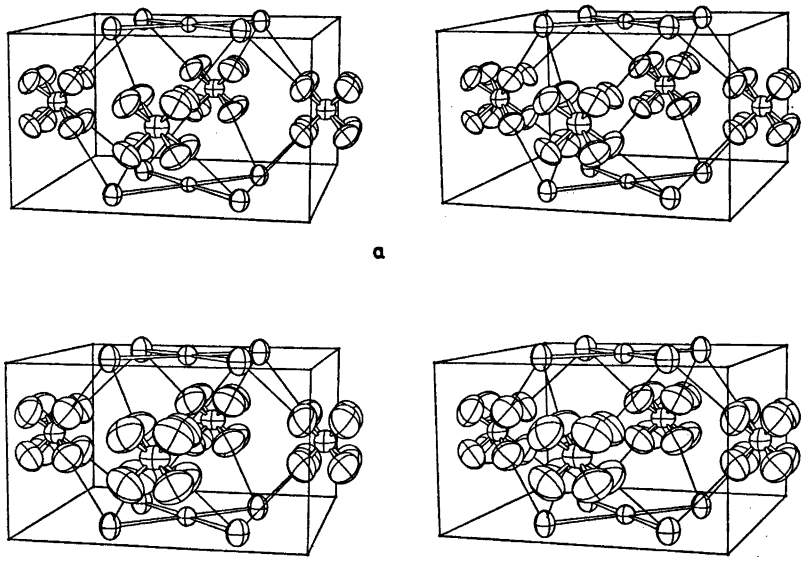

Fig. 1. Stereoscopic view of the molecular packing. The ammonium ion disorder appears as an arrangement of eight deuterium atoms around each nitrogen atom. N – D···Cl hydrogen bonds are shown as single line bonds, while N – D and Pd – Cl bonds are shown as double line bonds. (a) corresponds to the 125 K structure, and (b) to the 295 K structure. 50 % probability ellipsoids are shown.

corresponds to occupation 0.5 of two equally probable orientations of the ammonium ion creating two identical sets of hydrogen bonds N–D···Cl shown as single line bonds in Fig. 1. The hypothesis of disorder was tested in space group $P422$, which allows full occupation of either of the two above-mentioned orientations, and for either model the refinement was poorer at a highly significant level (at 125 K: $R(F)_{D1}=0.077$, $R(F)_{D2}=0.075$ as compared to $R(F)_{D1+D2}=0.040$ and at 295 K: $R(F)_{D1}=0.105$, $R(F)_{D2}=0.123$ as compared to $R(F)_{D1+D2}=0.074$). Due to the long counting times involved in diffraction methods, we cannot unambiguously state whether the disorder is static or dynamic, but should it be dynamic the ammonium groups spend little time in the transition phase as evidenced by a smooth final difference Fourier map. Thus, the ammonium ions are not *freely* rotating even at 295 K. This conclusion was also obtained by infrared spectroscopy on NH_3D^+ isotopically diluted crystals of $(NH_4)_2[PdCl_4]$.[10] It seems as if the N–H···Cl hydrogen bonds effectively hinder the rotation. However, our results do not allow a statement on the possibility of any weak correlation between the orientation of neighbouring ammonium ions, which in an instantaneous picture might correspond to the structure having locally adapted to one of the space groups favoured by Adams and Berg.[1] As an example, space group $P\bar{4}2m$ might be the adequate description of a low temperature instantaneous symmetry in ordered microdomains, in which fluctuations in time or space may average to give the overall symmetry $P4/mmm$. This difference in the symmetry deducible from diffraction and spectroscopic techniques is not a unique situation in molecular physics; *cf. e.g.*, the situation in $(NH_4)Br$.[11,12]

It is in principle possible to test the above speculations on the instantaneous symmetry by checking $(NH_4)_2[PdCl_4]$ crystals for second harmonic generation. If such an effect can be demonstrated at low temperatures, the centre of symmetry is absent.[13] The experiment is, however impeded [14] by the dark colour of the compound.

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