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Combined X-ray and Neutron Diffraction Study of $K_2[Pt(CN)_4]X_{0.3} \cdot 3H_2O$ with $X = Br, Cl$ (KCP) between 31 K and Room Temperature

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The results of six crystal structure refinements of $K_2[Pt(CN)_4]X_{0.3} \cdot 3H_2O$ with $X = Br, Cl$ (KCP) from X-ray and neutron diffraction measurements between 31 K and room temperature are presented and compared. Particular subjects of the discussion are the parameters of the $[Pt(CN)_4]$ groups, the distribution of the water molecules, and the temperature dependence of the temperature factors. The Pt–Pt distances deviate from each other by less than 0.007 Å. The $[Pt(CN)_4]$ groups are not planar. X-ray data show a correlation between the z parameters of the K atoms and (CN) groups. Zero-point vibrations and the magnitude of the positional disorder of the various atoms are derived from their temperature factors at different temperatures.

1. Introduction

The 'one-dimensional metal' $K_2[Pt(CN)_4]X_{0.3} \cdot 3H_2O$ ($X = Br, Cl$), abbreviated KCP, has attracted great attention in physical research (Zeller, 1973). Because the knowledge of its crystal structure is of fundamental importance to the understanding of its physical properties, we would like to present a critical summary of the main results of X-ray and neutron diffraction studies. In particular, a comparison of our new X-ray and neutron diffraction analyses at various temperatures has led us to definite statements concerning the behaviour of the water molecules. The dominant influence of the crystalline water on the electrical conductivity of KCP was recently shown by Drosdzik & Engbrodt (1975).

The first crystal structure determination (Krogmann & Hausen, 1968) based on film methods showed that 'one-dimensional metals' of the 'KCP-type' consist of linear Pt chains with unusually short Pt–Pt distances (2.89 Å). These chains run parallel to the c axis of the tetragonal cell. New X-ray and neutron structure investigations with counter methods (Deiseroth & Schulz, 1974; Williams, Petersen, Gerdes & Peterson, 1974) yielded a new space group of lower symmetry – $P4mm$ instead of $P4/mmm$ – and showed the K^+ ions to be not distributed statistically but arranged in ordered layers perpendicular to the Pt chains. Furthermore, the Pt atoms occupy two different atomic positions with variable z parameters. It is remarkable that they are equidistant within the possible limits of

error. This fact, which holds for all investigations made between 8 K and room temperature (Deiseroth & Schulz, 1974, 1975; Williams *et al.*, 1974; Heger, Renker, Deiseroth, Schulz & Scheiber, 1975; Peters & Eagen, 1976; Williams, Iwata, Ross, Petersen & Peterson, 1975; Williams, Ross, Iwata, Petersen, Peterson, Lin & Keefer, 1975), must be seen in connection with the very weak diffuse satellites (Comès, Lambert, Launois & Zeller, 1973; Comès, Lambert & Zeller, 1973; Renker, Pintschovius, Gläser, Rietschel, Comès, Liebert & Drexel, 1974). They indicate a sinusoidal distortion of the Pt atoms along the c axis (Peierls distortion), which is due to small displacements from their theoretical positions derived by classical structure analysis. Between 80 and 120 K an incomplete mutual ordering of the distorted Pt chains takes place (Renker *et al.*, 1974).

Some discussion was caused recently about a so-called additional Br site (Williams *et al.*, 1974). By studies on deuterated crystals (Heger *et al.*, 1975) it was clearly identified as an additional water position with a high degree of positional disorder and an occupation probability of about 0.4 (0.2 with respect to one formula unit). This result, which is in good agreement with thermal gravimetric studies (Peters & Eagen, 1975) and NMR measurements (Butler & Guggenheim, 1974; Brinkmann & Keller, 1975), gave rise to the assumption that the centre of the cell of KCP bromide is always occupied by either a Br atom or a water molecule.

Table 1. *Crystallographic data*

The Roman numbers (I)–(VI) refer to the data sets described in § 2. The lattice parameters are refined from the angular positions of 15 reflexions centred on the diffractometers. The standard deviations related to the last digits are given in parentheses. Reflexions were considered as observed if the threefold standard deviations of the intensity calculated from the count rates are lower than the net intensity. R and R_w refer to the conventional R and the weighted R value ($R = \sum |F_o| - |F_c| / \sum |F_o|$). The weights are calculated from counting statistics. Overall, even and odd refer to all reflexions and to reflexions with even and with odd l values respectively. R (unobserved) is the R value for the unobserved reflexions. For neutrons no separate R value calculations were performed for l even or odd.

	I	II	III	IV	V	VI
a (Å)	9.871 (3)	9.892 (6)	9.839 (6)	9.897 (6)	9.841 (6)	9.833 (6)
c (Å)	5.775 (2)	5.791 (4)	5.731 (4)	5.784 (4)	5.714 (4)	5.708 (4)
$\sin \theta/\lambda$ range (Å ⁻¹)	≤0.70	≤0.70	≤0.70	≤0.74	≤0.62	≤0.62
Number of symmetry-independent reflexions	529	528	516	417	371	365
Number of observations	345	372	427	417	371	365
R (overall)	0.019	0.017	0.029	0.032	0.034	0.043
R_w (overall)	0.019	0.019	0.030	0.044	0.051	0.065
R (l even)	0.015	0.014	0.023			
R_w (l even)	0.017	0.015	0.035			
R (l odd)	0.083	0.057	0.073			
R_w (l odd)	0.053	0.037	0.053			
R (unobserved)	0.46	0.55	0.64			

2. Experimental

In this paper we present and compare the results of the following six structure investigations: (I) KCP–Cl–H₂O at room temperature with X-rays, (II) KCP–Br–H₂O at room temperature with X-rays, (III) KCP–Br–H₂O at 90 K with X-rays, (IV) KCP–Br–D₂O at room temperature with neutrons, (V) KCP–Br–D₂O at 73.5 K with neutrons, (VI) KCP–Br–D₂O at 31 K with neutrons.

The results derived from these data sets have not been published (II and VI), have only partly been published (I and V) or have been published (Deiseroth & Schulz, 1975) with incorrect anisotropic temperature factors (III).^{*} All measurements were carried out by $\omega/2\theta$ scans on four-circle instruments (X-ray: Syntex P2₁, Mo K α ; neutrons: P32/FR2 Karlsruhe, $\lambda_n = 1.0327$ Å). The low-temperature measurements were performed with modified gas-flow equipment (LT1, Syntex) and a closed-cycle helium refrigerator (CS-1003, Air Products and Chemicals) in the case of X-ray and neutron diffraction respectively.

For the X-ray data, the atomic scattering factors of *International Tables for X-ray Crystallography* (1974) have been used for C, N, O, K⁺, Cl⁻, Br⁻ and Pt. The effect of anomalous dispersion in the X-ray measurements of KCP is practically of no importance for our refinements as we used averaged structure factors of Friedel pairs. For the refinement of the neutron diffraction data of deuterated KCP–Br the following

scattering lengths b (10⁻¹⁵ m) were used, taken from Willis (1973): $b_D = 6.67$, $b_C = 6.65$, $b_N = 9.40$, $b_O = 5.80$, $b_K = 3.70$, $b_{Br} = 6.79$ and $b_{Pt} = 9.40$. Because of the very small neutron cross-section for absorption of deuterated KCP no absorption correction was necessary. In our calculations no extinction effects were taken into consideration. Details of data collections and results of the structure refinements are summarized in Tables 1 and 2.* The derived crystal structure of KCP is illustrated in Fig. 1.

3. Results and discussion

It is our aim to compare all available results for KCP obtained from X-ray and neutron diffraction. In particular, we want to discuss the position of the [Pt(CN)₄] groups, the distribution of the water molecules and the temperature-dependent behaviour of the temperature factors.

3.1. [Pt(CN)₄] groups

The Pt atoms occupy the atomic positions (00z) with $z_1 = 0$ and $z_2 \approx 0.5$; thus they are able to form two different distances. The z coordinates of the Pt(2) atoms derived from four different X-ray studies [(I)–(III) and Peters & Eagen (1976)] are: (I) 0.4996 (4), (II) 0.4991 (3), (III) 0.4996 (4), Peters & Eagen

* The incorrect calculation of the anisotropic temperature factors (Deiseroth & Schulz, 1975) is because of an error which occurred in an earlier version of a structure analysis program system run on small computers.

* Lists of structure parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33083 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances (Å) and angles (°)*

The meanings of the data-set numbers are explained in § 2. The numbers in parentheses are the standard deviations related to the last digit.

	I	II	III	IV	V	VI
Pt(1)—Pt(2)						
Pt(1)—Pt(2)	2.883 (3)	2.889 (2)	2.863 (3)	2.894 (13)	2.853 (13)	2.837 (14)
Pt(2)—Pt(1)	2.892 (3)	2.902 (2)	2.868 (3)	2.890 (13)	2.860 (13)	2.871 (14)
Pt(1)—C(1)—N(1)						
Pt(1)—C(1)	2.005 (10)	2.004 (7)	2.011 (15)	1.995 (2)	1.991 (3)	1.990 (3)
C(1)—N(1)	1.155 (14)	1.153 (10)	1.138 (20)	1.157 (3)	1.166 (3)	1.167 (4)
C(1)—Pt(1)—C(1)	175 (1)	179 (1)	175 (1)	178 (1)	178 (1)	180 (1)
C(1)—Pt(1)—C(1)	89.9 (1)	90.0 (1)	89.9 (1)	90.0 (1)	90.0 (1)	90.0 (1)
Pt(1)—C(1)—N(1)	179 (2)	179 (2)	176 (2)	180 (1)	179 (1)	178 (1)
Pt(2)—C(2)—N(2)						
Pt(2)—C(2)	2.011 (5)	2.004 (4)	1.997 (7)	1.998 (1)	1.998 (1)	1.997 (1)
C(2)—N(2)	1.141 (7)	1.170 (6)	1.166 (10)	1.157 (1)	1.163 (2)	1.160 (2)
C(2)—Pt(2)—C(2)	179 (1)	179 (1)	174 (1)	179.6(7)	179.4 (8)	179.2 (7)
C(2)—Pt(2)—C(2)	90.0 (2)	90.0 (2)	89.9 (3)	90.0 (1)	90.0 (1)	90.0 (1)
Pt(2)—C(2)—N(2)	180 (2)	177 (2)	179 (2)	178 (1)	178 (1)	179 (1)
Cl or Br						
Cl—K or Br—K	3.31 (1)	3.33 (1)	3.33 (1)	3.35 (1)	3.33 (1)	3.33 (1)
Cl—O(2) or Br—O(2)	3.29 (3)	3.37 (2)	3.32 (2)	3.36 (1)	3.30 (1)	3.30 (1)
Br—D(2)				2.55 (2)	2.49 (2)	2.46 (2)
Water molecules						
O(1)—N(1)	2.99 (2)	2.96 (2)	2.89 (3)	2.99 (1)	2.97 (1)	2.96 (1)
O(1)—K	2.75 (2)	2.78 (1)	2.79 (2)	2.73 (1)	2.72 (1)	2.72 (1)
O(1)—D(1)				0.95 (1)	0.95 (1)	0.94 (1)
D(1)—O(1)—D(1)				101 (1)	102 (1)	102 (1)
O(2)—N(2)	2.97 (2)	3.05 (2)	3.04 (2)	2.99 (1)	2.99 (1)	2.99 (1)
O(2)—K	2.86 (1)	2.83 (1)	2.79 (2)	2.84 (1)	2.80 (1)	2.80 (1)
O(2)—D(2)				0.88 (6)	0.87 (3)	0.89 (2)
O(2)—D(3)				0.89 (5)	0.95 (2)	0.95 (5)
D(2)—O(2)—D(3)				100 (6)	102 (2)	102 (3)
O(3)—K	3.04 (2)	3.06 (1)	3.04 (2)	3.12 (1)	3.05 (1)	3.05 (1)
O(3)—O(2)	3.33 (6)	3.21 (6)	3.18 (7)	3.25 (1)	3.25 (1)	3.25 (1)
O(3)—D(4)				0.8 (2)	0.9 (3)	1.3 (3)
O(3)—D(5)				1.1 (2)	1.5 (4)	1.4 (4)
D(4)—O(3)—D(4)				61 (20)	103 (20)	136 (20)
D(4)—O(3)—D(5)				113 (20)	92 (20)	75 (20)
D(5)—O(3)—D(5)				74 (20)	75 (20)	74 (20)
K						
K—Cl or K—Br	3.31 (2)	3.33 (1)	3.33 (1)	3.35 (1)	3.33 (1)	3.33 (1)
K—O(1)	2.75 (1)	2.78 (1)	2.79 (2)	2.73 (1)	2.72 (1)	2.72 (1)
K—O(2)	2.86 (1)	2.83 (1)	2.79 (2)	2.84 (1)	2.80 (1)	2.80 (1)
K—O(3)	3.04 (2)	3.06 (1)	3.04 (2)	3.12 (1)	3.05 (1)	3.05 (1)
K—N(1)	3.01 (1)	2.99 (1)	2.97 (1)	3.00 (1)	2.96 (1)	2.96 (1)
K—N(2)				3.05 (4)	3.02 (4)	3.02 (4)

(1976) 0.4991 (2). Although in each single data set the z coordinates do not show significant deviations from $z = \frac{1}{2}$, if the standard deviations are taken into account, these four results together suggest a tendency for the z value of Pt(2) to be lower than $\frac{1}{2}$. Taking the mean of these four measurements, one obtains $z = 0.4994$ (3). The $z[\text{Pt}(2)]$ values derived from neutron measurements do not show a deviation from $z = \frac{1}{2}$, but these values are one order of magnitude less precise than the z values derived from X-ray studies.

All structure refinements in $P4mm$ show that the $[\text{Pt}(\text{CN})_4]$ groups are not planar, but there is a significant difference between X-ray and neutron diffraction data. It is obvious to assume a deviation from planarity by bending of the (CN) groups towards the K^+ layer, as shown schematically in Fig. 2(a). This means $z_1 > 0.0$ and $z_2 < 0.5$, for C(1), N(1) and C(2), N(2) respectively. This was found for all refinements of the neutron data [data sets (IV)–(VI) and Williams *et al.* (1974); Heger *et al.* (1975)]. However, for the X-ray data

another correlation was found between the z coordinates of the C, N and K^+ atoms which is shown in Figs. 2(b) and 3. These different pictures for the correlation of the $[Pt(CN)_4]$ groups and K^+ from X-ray and neutron diffraction analyses may be caused by a polarization of the electron distributions of the C and N atoms. A similar effect was not observed for the O and (Cl,Br) atoms.

3.2. Water distribution

As shown recently, there are three different water positions in the crystal structure of KCP (Heger,

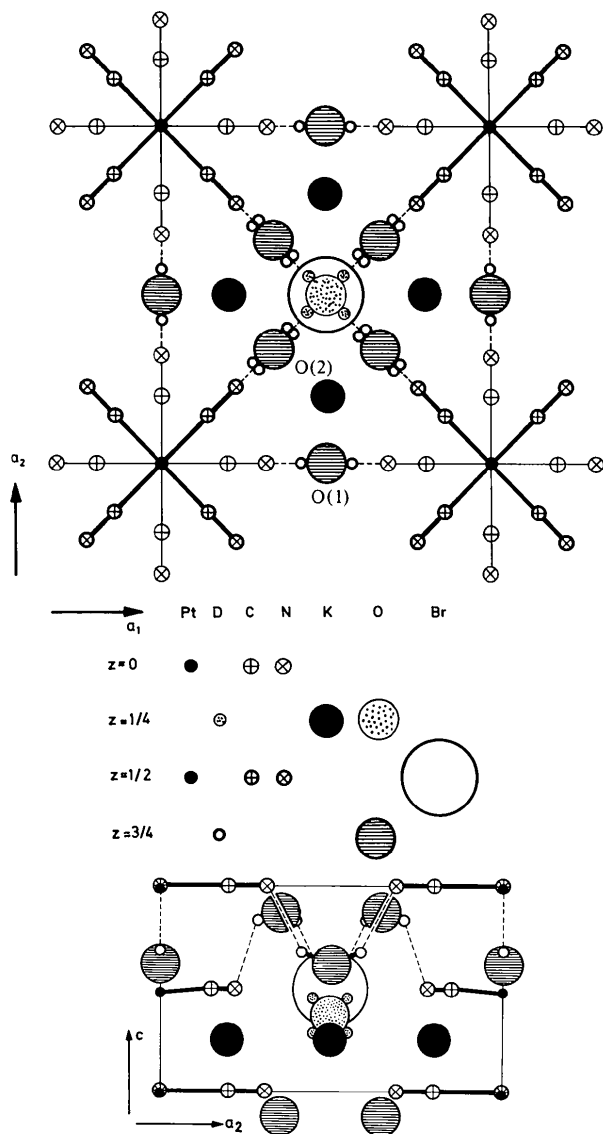


Fig. 1. Crystal structure of $K_2[Pt(CN)_4]Br_{0.3} \cdot 3D_2O$. Upper part: projection along the tetragonal c axis. Lower part: projection along one a axis.

Renker, Deiseroth & Schulz, 1976). This work aims in particular at studying the detailed behaviour of the water molecules between 31 and 295 K, *i.e.* in the interesting temperature range comprising the region of incomplete three-dimensional ordering between 80 and 120 K (Renker *et al.*, 1974). Combined X-ray and neutron diffraction investigations – especially those with fully deuterated samples – are a powerful tool for determining the positions, thermal-motion distributions, and occupation probabilities of water molecules.

$D_2O(1)$ is situated between neighbouring $[Pt(CN)_4]$ chains in the $[100]$ direction (Fig. 1). There are no anomalies, *i.e.* the O(1) and D(1) sites are fully

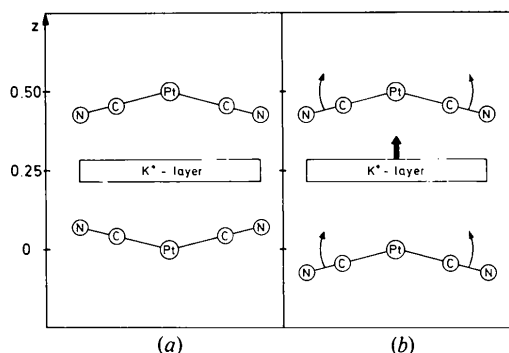


Fig. 2. Schematic representation of deviations from planarity of the $[Pt(CN)_4]$ groups (a) derived from neutron data, (b) derived from X-ray data. The directions of the arrows show the correlations between the z coordinates of the C, N and K^+ atoms.

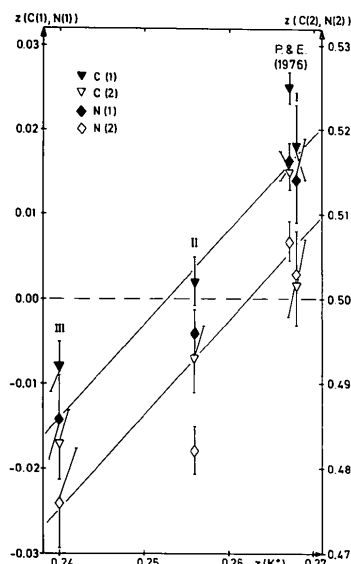


Fig. 3. Correlations between the z coordinates of the (CN) groups and the K^+ atoms derived from the X-ray data sets (I)–(III) and from Peters & Eagen (1976). The correlation lines give: $z[C(1), N(1)] = 1.1z(K^+) - 0.28$, and correlation coefficient $CC = 0.93$; $z[C(2), N(2)] = 1.03z(K^+) + 0.23$, and $CC = 0.89$.

occupied and their thermal parameters have relatively low values. For this 'regular' water molecule we found an O(1)—D(1) distance of 0.95 (1) Å and a D(1)—O(1)—D(1) angle of 102 (1)° independent of the special temperature under consideration.

D₂O(2), almost in the [110] direction, connects the [Pt(CN)₄] groups at $z \simeq 0.5$ and the halide ion in the centre of the unit cell (Fig. 1). It seems that this site is very sensitive to a reduction in the water content of KCP. For our deuterated sample crystals, stored and handled in a deuterated atmosphere of about 60% humidity (Kuse & Zeller, 1972), we found reduced occupation probabilities of 0.89 (4) [sample (I), used for the room-temperature measurements] and 0.80 (4) [sample (II), used for the low-temperature measurements].

At any temperature between 31 and 295 K this molecule is disordered and inclined by an angle of 16 (3)° with respect to [110] with the D(2)—D(3) connecting vector situated almost parallel to the (001) plane. Because of the very high thermal parameters of D(2) and D(3) we have to assume frequent reorientations between the two possible orientations of D₂O(2). As the O(2) atoms are not affected directly by this flipping, X-ray investigations cannot show clearly the disorder of this water molecule. However, the unusual discrepancies of thermal parameters and occupation probabilities determined by X-ray and neutron diffraction in the case of O(2) should be mentioned: the much higher X-ray values for these strongly correlated parameters suggest severe disordering effects. For all temperatures under consideration the D₂O(2) molecule has D—O(2) distances of 0.88 (4) Å [D(2)] and 0.95 (1) Å [D(3)] and a D(2)—O(2)—D(3) angle of 101 (3)°.

D₂O(3) fills the centre of the unit cell of KCP alternately with the halide ion (Fig. 1). Both X-ray and neutron diffraction yield an average occupation probability of 0.38 (4) for O(3). This value is significant for the amount of water in the unit-cell centres. The average halide occupancy deduced from X-ray and neutron analyses amounts to 0.59 (7). Thus, we can demonstrate our former conclusion once more by our experiments (Heger *et al.*, 1976) saying that the centre of the unit cell of KCP is always filled by either a halide ion or a water molecule.

Even by neutron diffraction with fully deuterated samples it is rather problematic to determine reliable parameters for the deuterons of D₂O(3), and it is still more questionable to make statements about changes in its behaviour under different temperature conditions. For all temperatures under consideration, besides the relatively fixed O(3) site, we have clear evidence for eight D(4)/D(5) positions leading to at least six different preferred orientations occupied statistically by this highly disordered water molecule with D—D vectors parallel or perpendicular to the *c* axis (Fig. 4).

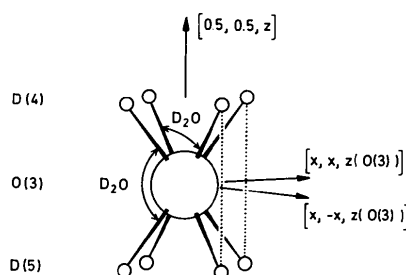


Fig. 4. Possible orientations of the D₂O(3) molecule. The eight D(4)/D(5) positions lead to at least six different preferred orientations occupied statistically with D—D vectors parallel or perpendicular to the *c* axis.

The reorientations between the different D₂O(3) orientations can be considered as hindered rotations around [0.5, 0.5, *z*]. With our diffraction analyses we were not able to prove a 'freezing out' effect on this rotation at low temperature (Brinkmann & Keller, 1975).

Our results on the behaviour of the water molecules in KCP should be compared with other information obtained by various experimental techniques. In the neutron diffraction studies we used two different crystals for the room-temperature (sample I) and low-temperature (sample II) measurements. Our analyses lead to a total water content per formula unit of 2.98 (12) for sample (I) and 2.78 (12) for sample (II). These values are smaller than the maximum possible water content of 3.2 per formula unit (Peters & Eagen, 1975) but they are in the range 2.5 to 3.1 resulting from various analyses (Cahen, 1973).

The various orientations of the water molecules determined by neutron diffraction can be compared with results from proton NMR measurements (Brinkmann & Maier, 1976) and infrared spectroscopy (Geserich, Möller, Scheiber & Überreiter, 1976). The non-diffraction methods yield water molecules with H—H vectors oriented parallel and perpendicular to the *c* axis. Regarding the H—H vectors parallel to *c*, the IR studies show that the corresponding water molecule should be the defect water H₂O(3). Taking all eight D(4) and D(5) positions found by our neutron analyses, D₂O(3) might also be orientated parallel as well as perpendicular to the *c* axis (Fig. 4). NMR work performed at room temperature reveals double rotation of this water molecule around [001] and [110]. With decreasing temperature, one degree of this rotation (around [110]) 'freezes' and H₂O orientations parallel to *c* will dominate (Brinkmann & Keller, 1975). It seems that these temperature-dependent dynamical and orientational properties of H₂O(3) do not alter significantly the preferred proton positions [D(4)/D(5) in our neutron studies].

Encouraged by the NMR results we split the D(2) and D(3) positions to take into account a positional disorder of D₂O(2). Besides a significant improvement

in the R values [R (293 K): 0.047 \rightarrow 0.032; R (73.5 K): 0.046 \rightarrow 0.034; R (31 K): 0.052 \rightarrow 0.043], an inclination angle of 16 (3) $^\circ$ with respect to [110] was found at all temperatures, which is in perfect accordance with the 16 (1) $^\circ$ from NMR (Brinkmann & Maier, 1976). The remaining high-temperature parameters for D(2) and D(3) might indicate further splitting of these positions, thus verifying totally the complicated NMR results. It should be mentioned that this short summary was based on the assumption that the water positions (2) and (3) were incorrectly identified in the NMR work (Brinkmann & Maier, 1976). If the sites (2) and (3) are interchanged, all information available on the individual orientations of the different water molecules in KCP is in accordance with our model.

3.3. Temperature dependence of the temperature factors

Fig. 5 shows the temperature dependence of the isotropic u values. The temperature variation is taken as a linear function. The isotropic temperature factor TF has been refined in the form: $TF = \exp[-8\pi^2 u(\sin \theta/\lambda)^2]$. The mean square displacement u can be written $u = U_0^2 + U_d^2 + U_t^2$. U_0^2 is the displacement caused by the zero-point energy. U_d^2 is caused by a positional disorder, if only a so-called 'point of gravity' position is refined for this atom (Schulz, 1972). U_t^2 is the mean square displacement according to the usual Debye-Waller factor. Only U_t^2 depends on the temperature: $U_t^2 = KTQ(\theta/T)/(m_A \theta^2)$, where T : absolute temperature; θ : Debye temperature; Q : Debye function; K : proportionality factor.

The linear variation of U_t^2 with T found means that

$$Q(\theta/T)/\theta^2 = \text{constant.}$$

In the lower part of Fig. 5 all atoms are shown which are expected to have no positional disorder or only a very small U_d^2 value, which is caused by the Peierls distortion. Taking the U_0^2 values of Fig. 5 [$U_0^2 = u(T = 0 \text{ K})$], it is found that the values of $U_t^2/U_0^2 T$ lie between 0.9 and 1.2. Furthermore, it follows that the deviations of the Pt atoms from their average positions on account of the Peierls distortion must be smaller than 0.042 Å. In the upper part of Fig. 5 those atoms are shown which may have positional disorder: the O and the D atoms.

It is found that O(1) has the same U_0^2/U_t^2 ratio as all the other ordered atoms. Also, the temperature factors of O(2) and O(3) derived from neutron data follow this line; however, the corresponding X-ray values lie on another straight line which is shifted parallel to the O(1) line. The difference of the corresponding u values at $T = 0$ [$u(T = 0 \text{ K}) = U_0^2 + U_d^2$] corresponds to $U_d = 0.17$ Å of the electronic shell of these two atoms. The B values of D(1), on the one hand, and D(2) and D(3), on the other hand, also lie on straight lines, which are shifted in parallel (upper part of Fig. 5). If we assume that D(1) has no positional disorder, we can estimate $U_d = 0.19$ Å for D(2) and D(3) atoms.

4. Conclusions

By our combined X-ray and neutron diffraction study performed at temperatures between 31 and 295 K we have derived a detailed picture of the structural properties of KCP. This confirms all relevant information from earlier structure analyses, *i.e.* almost equal Pt–Pt distances, nonplanarity of the $[Pt(CN)_4]$ groups, alternate filling of the unit-cell centres by halide ions or water molecules. In addition, we report the following new results: (1) correlation was found between the electron-density distributions of the K^+ ions and the

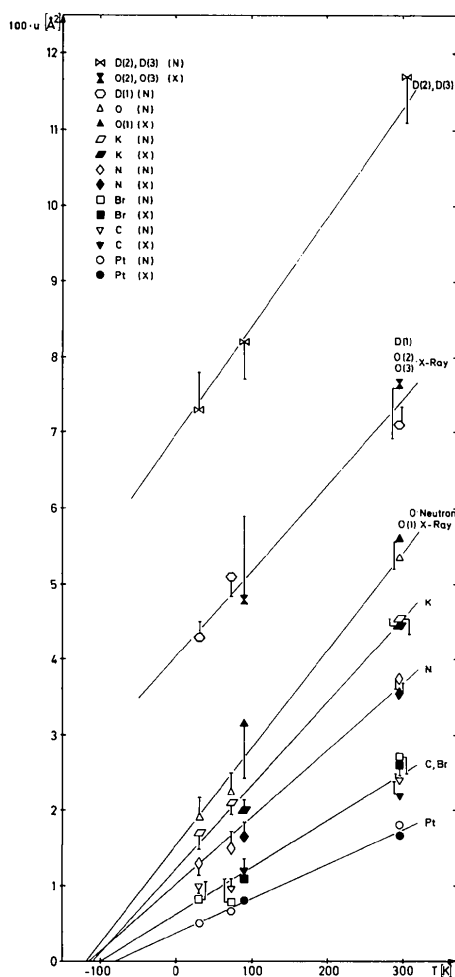


Fig. 5. Temperature dependence of the isotropic temperature factors. The temperature factors of the following atoms have been averaged: Pt, C, N; O(neutron); O(2) and O(3) (X-ray); D(2) and D(3) (neutron). The error bars point only into the direction of the corresponding straight line. When it was possible, the temperature variation for several atoms has been represented by one line in order to avoid overcrowding of the figure.

(CN) groups; (2) in addition to the occupational disorder of D₂O(2), a positional disorder of its D atoms exists which leads to an inclination of the corresponding D—D vectors by an angle of 16° with respect to the [110] direction; (3) at all temperatures under consideration the D—D vectors of the central water molecules D₂O(3) may be oriented parallel or perpendicular to the *c* axis; (4) from the temperature dependence of the temperature factors we determined the magnitude of the zero-point vibration of all atoms as well as of the positional disorder of the water molecules (2) and (3).

We would like to thank G. Scheiber of Karlsruhe University for providing us with deuterated KCP crystals and Professor Dr K. Krogmann of Karlsruhe University for synthesizing the KCP crystals used in the X-ray measurements. Finally, we thank Dr B. Renker for his stimulating interest and helpful discussions.

References

- BRINKMANN, D. & KELLER, H. U. (1975). *Phys. Status Solidi B*, **67**, K42–K46.
- BRINKMANN, D. & MAIER, K. (1976). *Solid State Commun.* **19**, 1099–1103.
- BUTLER, M. A. & GUGGENHEIM, H. J. (1974). *Phys. Rev. B*, **10**, 1778–1783.
- CAHEN, D. (1973). *Solid State Commun.* **12**, 1091–1094.
- COMÈS, R., LAMBERT, M., LAUNOIS, H. & ZELLER, H. R. (1973). *Phys. Rev. B*, **8**, 571–575.
- COMÈS, R., LAMBERT, M. & ZELLER, H. R. (1973). *Phys. Status Solidi B*, **58**, 578–592.
- DEISEROTH, H. J. & SCHULZ, H. (1974). *Phys. Rev. Lett.* **33**, 963–965.
- DEISEROTH, H. J. & SCHULZ, H. (1975). *Mater. Res. Bull.* **10**, 225–228.
- DROSDZIOK, S. & ENGBRODT, M. (1975). *Phys. Status Solidi B*, **72**, 739–742.
- GESERICH, H. P., MÖLLER, W., SCHEIBER, G. & ÜBERREITER, B. (1976). *Verh. Dtsch. Phys. Ges.* (VI), **11**, 531.
- HEGER, G., RENKER, B., DEISEROTH, H. J. & SCHULZ, H. (1976). *Solid State Commun.* **18**, 517–519.
- HEGER, G., RENKER, B., DEISEROTH, H. J., SCHULZ, H. & SCHEIBER, G. (1975). *Mater. Res. Bull.* **10**, 217–224.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
- KROGMANN, K. & HAUSEN, H.-D. (1968). *Z. Anorg. Allg. Chem.* **358**, 67–81.
- KUSE, D. & ZELLER, H. R. (1972). *Solid State Commun.* **11**, 355–359.
- PETERS, C. & EAGEN, C. F. (1975). *Phys. Rev. Lett.* **34**, 1132–1134.
- PETERS, C. & EAGEN, C. F. (1976). *Inorg. Chem.* **15**, 782–788.
- RENKER, B., PINTSCHOVIVUS, L., GLÄSER, W., RIETSCHEL, H., COMÈS, R., LIEBERT, L. & DREXEL, W. (1974). *Phys. Rev. Lett.* **32**, 836–839.
- SCHULZ, H. (1972). *Z. Kristallogr.* **136**, 321–329.
- WILLIAMS, J. M., IWATA, M., ROSS, F. K., PETERSEN, J. L. & PETERSON, S. W. (1975). *Mater. Res. Bull.* **10**, 411–416.
- WILLIAMS, J. M., PETERSEN, J. L., GERDES, H. M. & PETERSON, S. W. (1974). *Phys. Rev. Lett.* **33**, 1079–1081.
- WILLIAMS, J. M., ROSS, F. K., IWATA, M., PETERSEN, J. L., PETERSON, S. W., LIN, S. C. & KEEFER, K. (1975). *Solid State Commun.* **17**, 45–48.
- WILLIS, B. T. M. (1973). *Chemical Application of Thermal Neutron Scattering*, pp. 296–299. Oxford Univ. Press.
- ZELLER, H. R. (1973). *Festkörperprobleme XIII*, edited by H. J. QUEISSER, p. 31. Braunschweig: Pergamon/Viehweg.