

# Intermolecular Effects on the Geometry of $[\text{PtCl}_4]^{2-}$ . X-Ray Diffraction Studies of Aqueous $\text{H}_2\text{PtCl}_4$ and Crystalline $(\text{NH}_4)_2\text{PtCl}_4$

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The structure of  $[\text{PtCl}_4]^{2-}$  has been determined in an aqueous solution of 1.20 M  $\text{H}_2\text{PtCl}_4$  and 0.7 M HCl using the LAXS technique. Pt(II) is coordinated to four Cl in a square-planar configuration with a Pt-Cl distance of 2.32(1) Å.

The crystal structure of  $(\text{NH}_4)_2\text{PtCl}_4$  has been determined from X-ray single-crystal intensity data collected at room temperature with a CAD4 diffractometer. Crystal data at room temperature (MoK $\alpha$ ;  $\lambda = 0.7107$  Å) are:  $M_r = 372.98$ , tetragonal,  $P4/mmm$ ,  $Z = 1$ ,  $a = 7.1525(9)$ ,  $c = 4.2979(5)$  Å,  $V = 219.88(5)$  Å<sup>3</sup>,  $D_x = 2.817$  g cm<sup>-3</sup> and  $\mu = 17.26$  mm<sup>-1</sup>. The refinement converged to  $R = 0.0275$  for 750 reflexions with  $I > 2\sigma(I)$ .

The structure is composed of pseudotetrahedral  $\text{NH}_4^+$  and square-planar  $\text{PtCl}_4^{2-}$  ions linked by hydrogen bonds N-H...Cl with an N...Cl distance of 3.326(1) Å. However, the hydrogen atoms are disordered, corresponding to two equally probable orientations of the ammonium ion with two identical sets of hydrogen bonds. The Pt-Cl bond length, 2.305(1) Å, is not significantly different from the corresponding distance in solution, 2.32(1) Å.

A literature survey of accurate crystal structure determinations of  $\text{PtCl}_4^{2-}$  gives an average Pt-Cl distance of 2.304(7) Å; it is thus concluded that the geometry is very rigid, but variations due to intermolecular forces are slightly above the noise level of experimental errors for very accurate crystal structure determinations.

The experimentally observed variation of a bond distance M-X, in a metal complex  $\text{MXL}_n$ , is due to intra- and intermolecular forces as well as experimental errors. We have previously shown that for geometries based on single-crystal X-ray data variations due to intramolecular forces, such as *cis*- and *trans*-influences, in some cases are well above the 'noise level' of variations due to intermolecular forces and experimental errors.<sup>1-3</sup> In an attempt to discriminate between variations due to effects of intermolecular forces *contra* experimental errors we have chosen the  $\text{PtCl}_4^{2-}$  system, since this ion often has high symmetry and the bond distances consequently can be determined with high accuracy and precision. The geometry of this complex is reported in the literature for 10 crystal structure determinations based on diffractometer data.<sup>4-12</sup> The average,  $\langle d \rangle$ , and dispersion,  $\sigma$ , of the Pt-Cl distance are 2.304 and 0.007 Å, respectively. The dispersion is calculated from  $\sigma = [\Sigma(d - \langle d \rangle)^2 / (n - 1)]^{1/2}$ , where  $n$  is the number of distances. In Millon's salt,  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ , each Cl accepts two hydrogen bonds of the type N-H...Cl. In spite of this fact, the Pt-Cl bond is only 2.298(4) Å.<sup>7</sup> Equally short Pt-Cl distances, 2.296(7)-2.298(6) Å, for hydrogen-bond-accepting chlorine atoms are observed in  $[\text{Ir}(\text{NH}_3)_5\text{Cl}][\text{PtCl}_4]$ ,<sup>10</sup> and in  $[\text{PtCl}_2(\text{C}_3\text{H}_{10}\text{N}_2)_2][\text{PtCl}_4]$  they are only slightly longer.<sup>11</sup> In one compound,  $[\text{NPr}^n]_2\{[\text{PtCl}_4]_{\text{cis}}$

$[\text{PtCl}_2\text{NH}_2\text{Me}]_2\}$ , a Pt-Cl distance of 2.314 Å<sup>12</sup> for a hydrogen-bond-accepting chlorine is observed. This distance is significantly larger than an average distance including non-hydrogen-bonded Pt-Cl distances as well. The Pt-Cl bond seems very rigid, and is only slightly affected by hydrogen bonding and other intermolecular forces. For this reason we decided to make a complete crystal structure determination of the compound  $(\text{NH}_4)_2[\text{PtCl}_4]$ , in which there most probably are hydrogen bonds of the type N-H...Cl.

In a dynamic liquid one would expect a dramatically different influence on  $\text{PtCl}_4^{2-}$  from the medium compared to that in a solid. The structure of an 1 M aqueous solution of  $(\text{NH}_4)_2\text{PtCl}_4$  has previously been studied by Johansson using a large-angle X-ray scattering technique (LAXS).<sup>13</sup> The observed Pt-Cl distance, 2.31 Å, is equal to the average for the 10 crystal structure determinations, in spite of the fact that this distance inevitably must be influenced by hydrogen bonding of the type O-H...Cl. Johansson

Table 1. The concentrations, stoichiometric volume, density and linear absorption coefficient in the  $\text{H}_2\text{PtCl}_4$  solution studied by liquid X-ray scattering.

$C_{\text{Pt}}/\text{M}$	$C_{\text{Cl}}/\text{M}$	$C_{\text{O}}$	$C_{\text{H}}/\text{M}$	$V/\text{Å}^3$	$\rho/\text{g cm}^{-3}$	$\mu/\text{cm}^{-1}\text{M}^{-1}$
1.20	5.50	46.68	93.35	1384	1.27	29.7

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Table 2. Positional and isotropic thermal parameters for crystalline  $(\text{NH}_4)_2[\text{PtCl}_4]$ ; e.s.d.s in parentheses.

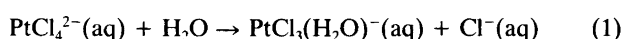
Atom	$x/a$	$y/b$	$c/b$	$U_{\text{iso}}/10^{-2} \text{ \AA}^2$ <sup>a</sup>
Pt	0.0	0.0	0.0	2.10(1)
Cl	0.227 89(12)	0.227 89(12)	0.0	3.15(3)
N	0.0	0.5	0.5	3.42(20)
H	0.071(11)	0.442(12)	0.369(16)	4.8(3.5)

<sup>a</sup>For the non-hydrogen atoms  $U_{\text{iso}}$  has been calculated from the average of the anisotropic temperature factors.

claims<sup>13</sup> that the Pt–Cl distances with this experimental method can be determined with an accuracy and precision equal to a corresponding crystal structure determination. However, considering the amounts of approximate corrections applied to the experimental data, this statement could be somewhat optimistic. It may still be fruitful to include structure determinations in solution in a discussion of the effect of intermolecular forces on the geometry of the  $\text{PtCl}_4^{2-}$  ion. It was therefore considered of interest to make a redetermination of the geometry of  $\text{PtCl}_4^{2-}$  in a solution with a composition different to 1 M  $(\text{NH}_4)_2\text{PtCl}_4$ , using the LAXS technique.

### Experimental

**$\text{H}_2\text{PtCl}_4$  solution.** A saturated aqueous solution of  $\text{K}_2\text{PtCl}_4$  (12.45 g  $\text{K}_2\text{PtCl}_4$  in 70 ml aqueous solution) was passed through a column of a  $\text{H}^+$ -saturated cation exchanger (Dowex 50W-X8). Part of the solution was evaporated (heat lamp) to a final volume of 25.00 ml. During this process three portions of 1 ml each of concentrated hydrochloric acid were added in order to avoid the ligand exchange reaction (1). The equilibrium constant is 0.013 at 25 °C.<sup>14</sup>



The concentration of Pt(II) was determined spectrophotometrically as  $\text{PtCl}_4^{2-}$ , and the total concentration of chloride gravimetrically with a method similar to the one

Table 3. The interatomic distances,  $D$ , temperature factors,  $B$ , and the number of distances,  $N$ , obtained from a least-squares analysis of the liquid X-ray scattering data.<sup>a</sup>

Distance	$D/\text{ \AA}$	$B/\text{ \AA}^2$	$N$	
Pt–Cl	2.32(1)	0.0029(9)	4.2(2)	per platinum
Cl–Cl <sub>cis</sub>	3.18(8)	0.01(1)	4(2)	per platinum
Cl–Cl <sub>trans</sub>	4.64 (fixed)	0.02 (fixed)	2.0 (fixed)	per platinum
Cl–O	3.58(7)	0.02(1)	5(1)	per chloride
O–O <sub>i</sub>	2.85(3)	0.044(7)	4.4(5)	per water molecule
O–O <sub>ii</sub>	4.46(7)	0.06(2)	3.1(7)	per water molecule

<sup>a</sup>The parameters were used in the calculations of the theoretical lineshapes in Figs. 1(a) and (b). The errors in parentheses correspond to one mean error.

for preparation of  $\text{Pt}(\text{H}_2\text{O})_2^{2+}(\text{aq})$ .<sup>15</sup> The results are given in Table 1, together with some physical parameters of the solution.

**Crystals of  $(\text{NH}_4)_2[\text{PtCl}_4]$ .** Dark-red single crystals of  $(\text{NH}_4)_2[\text{PtCl}_4]$  were obtained by slow evaporation of a  $(\text{NH}_4)_2\text{PtCl}_4$  solution at room temperature. The solution was prepared by the same ion exchange technique as described above, but with an  $\text{NH}_4^+$ -saturated ion exchanger.

**Liquid X-ray scattering.** A large-angle  $\theta$ – $\theta$  GSD Seifert diffractometer was used to register the scattering of MoK $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) from the free surface of the solution, employing a curved LiF monochromator of the Johansson type. In order to avoid evaporation of water and hydrogen chloride, the solution was kept in a calibrated thin-walled cylindrical glass container during the whole experiment. The scattering was recorded at discrete scattering angles,  $2\theta$ , collecting in total  $8 \times 10^4$  counts between 8 and  $70^\circ$  and  $4 \times 10^4$  counts in the range  $70$ – $106^\circ$  in at least two separate scans in order to check the reproducibility. The scattering data from the angle region  $1$ – $8^\circ$ , hidden by the upward meniscus in the glass container, was obtained

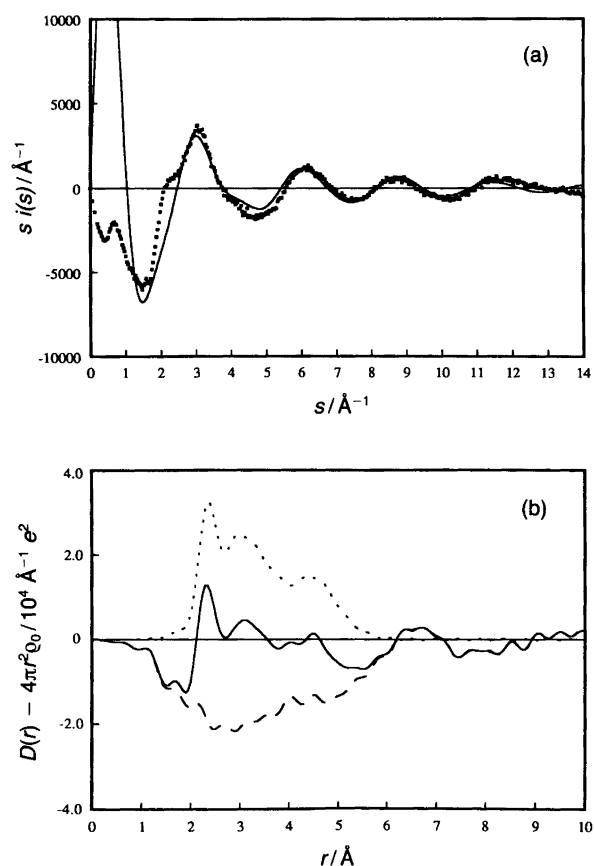


Fig. 1. The experimental results and theoretical model for the aqueous solution investigated by liquid X-ray scattering: (a) the reduced intensity function of the theoretical model and experimental points; (b) the experimental rPDF (---) and the theoretical peak shapes calculated from the parameters given in Table 3 (····), and their difference (—).

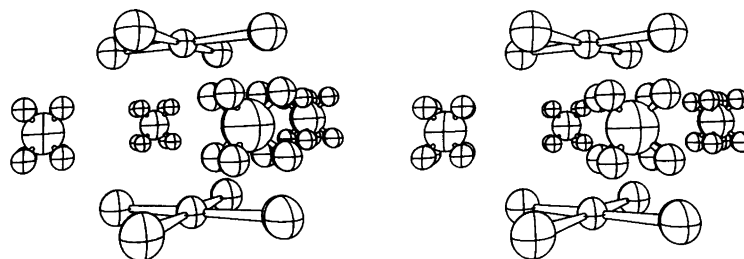


Fig. 2. Packing diagram of  $(\text{NH}_4)_2[\text{PtCl}_4]$ . The disorder of the ammonium ion appears as an arrangement of eight hydrogen atoms around each nitrogen atom.

separately; the scattered radiation was recorded from the solution in an open Teflon container (only 5000 counts in one scan). The evaporation during this procedure was negligible. The increment between scattering angles was in all scans 0.0335 in  $s$ , defined from  $s = 4\pi\lambda^{-1}\sin\theta$ .

The corrections and data treatment have been described in detail elsewhere.<sup>16–20</sup> The experimental intensity data were normalized to a stoichiometric volume,  $V$ , containing one platinum atom. The scattering factors for coherent and incoherent scattering were taken from Refs. 21–23. Spurious peaks below 1 Å, not corresponding to any interatomic distances, were removed by a Fourier retransformation procedure.<sup>16</sup> The computer programs KURVLR and STEPLR were used in the calculations.<sup>24,25</sup>

**Single-crystal X-ray data.** A crystal of dimensions 0.125×0.25×0.312 mm was used for data collection at room temperature with a CAD4 diffractometer employing graphite monochromatised  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107$  Å). The Laue class is  $4/mmm$ . No observed systematic extinctions are consistent with the space groups  $P422$ ,  $P4mm$ ,  $P42m2$ ,  $P4m2$  and  $P4/mmm$ . The space group of the highest symmetry,  $P4/mmm$ , was chosen for all calculations. Unit-cell dimensions were determined by least-squares calculations from 25  $\theta$ -angles measured on the diffractometer as  $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}l})/2$ ;  $a = 7.1525(9)$ ,  $c = 4.2979(5)$  Å,  $V = 219.88(5)$  Å<sup>3</sup>,  $Z = 1$ . The intensities of 750 reflections in one quarter of the reflection sphere,  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 10$ ,  $0 \leq l \leq 6$  obeying  $3.0 \leq \theta \leq 30.0^\circ$ , were measured with  $\omega$ - $2\theta$  scan ( $\Delta\omega = 1.3^\circ + 0.5^\circ \tan\theta$ ). The scan interval was extended by 25% at both ends for the background measurements. The ratio  $\sigma(I)/I$  requested in a scan was 0.028, and the maximum recording time was 150 s. The variation in three standard reflections was less than 2%.  $I$  and  $\sigma(I)$  were corrected for Lorentz, polarization and absorption effects ( $\mu = 17.26$  mm<sup>-1</sup>, transmission factors 0.0173–0.1406). All 750 reflections obeyed  $I > 2\sigma(I)$  and were used in the calculations. The structure was solved by Patterson and difference Fourier methods assuming the space group  $P4/mmm$ . In this space group the hydrogens are located in the general position with 16-fold degeneracy, which implies an occupancy of 0.5. The ammonium ion thus has two different orientations in this description. The structure is isotopic with  $(\text{ND}_4)_2[\text{PdCl}_4]$ , which was studied

by Larsen *et al.*<sup>26</sup> at low and ambient temperatures using neutron diffraction. They tested the possibility of removing the disorder by refining in the space groups of lower symmetry. However, they found no improvements in the refinements. Since the positions of the hydrogen atoms are much less accurately determined in our X-ray experiment, there is no reason to choose a space group of lower symmetry. In the final cycles of full-matrix least-squares, with Pt, Cl and N anisotropically and H isotropically refined, the weights were calculated from  $w^{-1} = \sigma^2(|F_o|) + (0.028|F_o|)^2 + 0.26$ . The function  $\Sigma w(|F_o| - |F_c|)^2$  was minimized. The final  $R$ -values obtained were  $R = 0.0275$  and  $R_w = 0.0368$ . A  $\delta R$ -plot gives a straight line with a slope of 1.0 and an intercept at  $-0.03$ . Scattering factors with corrections for anomalous dispersion were taken from Ref. 21. The maximum electron density in a final difference Fourier calculation,  $1.8$  e Å<sup>-3</sup>, was located close to the Pt atom. Tables of  $|F_o|$ ,  $\sigma(|F_o|)$  and  $|F_c|$  are available on request from the authors. The computer programs used were those compiled and amended by Lundgren.<sup>27</sup> Final atomic parameters are given in Table 2.

## Results

**Liquid X-ray scattering.** The reduced intensity function and reduced radial distribution function (rRDF) are shown in Figs. 1(a) and (b), respectively. The predominant features in the rRDF are the peaks about 2.3, 3.0–3.5 and 4.0–4.5 Å. These results agree qualitatively well with those previously obtained for aqueous solutions of  $\text{HAuCl}_4$ ,  $\text{HAuBr}_4$  and  $(\text{NH}_4)_2\text{PtCl}_4$ .<sup>13,28</sup> The first peak at 2.3 Å corresponds to the Pt–Cl distance in  $\text{PtCl}_4^{2-}$  complexes. The second peak consists of contributions from the nearest-neighbour interactions in the water structure about 2.8 Å and *cis*-Cl–Cl distances in  $\text{PtCl}_4^{2-}$ , as well as Cl–O contacts from both complex-bound and free chloride ions.<sup>29–31</sup> The

Table 4. Distances (in Å) and angles (in °) for crystalline  $(\text{NH}_4)_2[\text{PtCl}_4]$ .

Pt–Cl	2.305(1)	Cl–Pt–Cl	90.0
N–H	0.87(8)	H–N–H	99(9)
H⋯Cl	2.27(8)	N–H⋯Cl	169(7)
N⋯Cl	3.3261(3)		

Table 5. Pt–Cl distances (in Å) observed in the complex  $[\text{PtCl}_4]^{2-}$  in solid state and in solution.

Compound	$d_{\text{Pt-Cl}}/\text{Å}$	Comments	Ref.
$\text{K}_2[\text{PtCl}_4]$	2.308(2)		4
$\text{K}_2[\text{PtCl}_4]$	2.310(1)	X-Ray data	5
	2.309(1)	Neutron data	
$\text{K}_2[\text{PtCl}_4]$	2.309(1)		6
$[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$	2.298(4)	Hydrogen-bonded	7
$\text{Cs}_2[\text{PtCl}_4]$	2.294		8
	2.305		
$[\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2]_2[\text{PtCl}_4]$	2.313(1)		9
	2.305(1)		
$[\text{Ir}(\text{NH}_3)_5\text{Cl}][\text{PtCl}_4]$	2.298(6)	Hydrogen-bonded	10
	2.296(7)	Hydrogen-bonded	
	2.314(8)		
$[\text{PtCl}_2(\text{C}_3\text{H}_{10}\text{N}_2)_2][\text{PtCl}_4]$	2.305(2)	Hydrogen-bonded	11
	2.306(1)	Hydrogen-bonded	
$[\text{NPr}^i_4]_2\{[\text{PtCl}_4]_{\text{cis}}[\text{PtCl}_2\text{NH}_2\text{Me}]_2\}$	2.303		12
	2.291		
	2.294		
	2.314	Hydrogen-bonded	
$(\text{NH}_4)_2[\text{PtCl}_4]$	2.305(1)	Hydrogen-bonded	This study
1 M $(\text{NH}_4)_2\text{PtCl}_4$	2.31	Aqueous solution	13
1.2 M $\text{H}_2\text{PtCl}_4$	2.32(1)	Aqueous solution	This study

third peak is composed of all sorts of second coordination sphere separations, involving contributions from Pt–O, water O–O, as well as *trans*-Cl–Cl correlations in the tetrachloro complex. The final results of least-squares analyses of the experimental data in the range  $s = 3\text{--}14 \text{ \AA}^{-1}$  are shown in Table 3. Focusing on the short-range distances, e.g. Pt–Cl, by using  $s = 5\text{--}14 \text{ \AA}^{-1}$ , does not alter the results within experimental error. The applied weighting function,  $w(s)$ , was proportional to  $\cos \theta / [I(s)]^2$ . The assignment of atom–atom correlations to the long-distance peak about 4.0–4.5 Å is essentially arbitrary. Only *trans*-Cl–Cl and second-order water O–O distances were applied in the numerical analysis. Although other contributions may be of importance, no accurate assignment can be made from one X-ray scattering experiment alone. Furthermore, the primary interest is to reproduce a reasonable theoretical lineshape to support the quantitative evaluation of the parameters of the short Pt–Cl interactions.

*The crystal structure of  $(\text{NH}_4)_2[\text{PtCl}_4]$ .* The structure is isotopic with  $\text{M}_2[\text{PdCl}_4]$  ( $\text{M} = \text{NH}_4^+$ ,  $\text{ND}_4^+$  and  $\text{K}^+$ ) and  $\text{K}_2\text{PtCl}_4$ . The molecular packing is depicted in Fig. 2 and selected bond distances and angles are given in Table 4. The structure is composed of layers of square-planar complexes  $[\text{PtCl}_4]^{2-}$ . The layers are intercalated by  $\text{NH}_4^+$  ions in such a way that a three-dimensional hydrogen-bond network of almost linear bonds  $\text{N–H}\cdots\text{Cl}$ ,  $169(7)^\circ$ , is formed. Each ammonium ion is surrounded by eight chlorine neighbours at the corners of a rectangular prism. Since the hydrogen atoms in this space group are placed in a 16-fold position the occupancy of each site is 0.5 and the ammonium ion has two equally probable orientations. Two identical sets of hydrogen bonds  $\text{N–H}\cdots\text{Cl}$  are thus created. Each Cl has four ammonium ions as neighbours, but since

this ion has two equally probable orientations, each Cl accepts, on average, two hydrogen bonds.

## Discussion

Pt–Cl distances of the complex  $[\text{PtCl}_4]^{2-}$  from eleven crystal structure and two X-ray structure determinations in solution are given in Table 5. There are four studies of  $\text{K}_2\text{PtCl}_4$ , three applying X-ray and one neutron diffraction. The distribution of the Pt–Cl distance in these compounds is only affected by experimental errors, systematic and random. The narrow range observed for these distances, 2.308–2.310 Å, implies that the expectation value for the Pt–Cl distance in  $\text{K}_2\text{PtCl}_4$  is in the range 2.306–2.312 Å for a 95% confidence interval. On the assumption that the experimental errors are roughly the same for all of the crystal structure determinations, the range observed, 2.294–2.314 Å, indicates that that intermolecular forces perturbate the geometry slightly above the ‘noise level’ of experimental errors. This anticipation is also supported by the larger dispersion calculated as one  $\sigma$  comparing the four  $\text{K}_2\text{PtCl}_4$  structures alone (0.0008 Å) and all crystal structures included (0.007 Å). However, the total variation is small, and the average value for all crystal structures, 2.304(7) Å, is a suitable reference value in a discussion of the effect of intramolecular forces on the Pt–Cl bond distance.<sup>2</sup> It is remarkable that with one exception, 2.314 Å, the distances affected by hydrogen bonds  $\text{N–H}\cdots\text{Cl}$  are roughly equal to or shorter than the average value, 2.304(7) Å. The Pt–Cl distances observed in the two solution structure determinations are not significantly different. However, in 1 M  $(\text{NH}_4)_2\text{PtCl}_4$  the concentration of the interfering complex  $[\text{PtCl}_3(\text{H}_2\text{O})]$  is more than 0.1 M, compared to about 0.02 M in 1.2 M  $\text{H}_2\text{PtCl}_4$  with a 0.7 M

excess of HCl. Equilibrium data from Ref. 12 have been employed. The presence of the monoaquated complex will certainly introduce a systematic error showing up as an underestimated Pt-Cl distance. Unfortunately, the experimental errors in the solution structure determinations are too large to allow any decisive conclusions about the effects of intermolecular forces on the bond distance.

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