4. Standard deviations calculated by standard procedures for case (*a*) are given, and demonstrate the inappropriateness of scaling weights to make $\Sigma\, w\Delta^2/(n-m)=1$ for error estimation when systematic errors occur in the assigning of relative weights.

The improvement in the ranges of comparable bond lengths for (*b*) is obvious for the Zn–O and O–C distances, and while this is not so for the C–C distances, the mean C–C distance is much more realistic. A systematic error in the data was reduced by excluding certain reflexions. However, the error still remains and its unknown covariance with the refined parameters has caused an underestimate of standard deviations. This characteristic is discussed by Rae (1975).

The structure consists of two-dimensional polymer sheets perpendicular to (100). Zn atoms at x,y,z and x, $1+y$, z are linked by one propionate group and Zn atoms at x,y,z and $x,\frac{1}{2}-y,\frac{1}{2}+z$ by the other (Fig. 1).

The Zn atoms have a tetrahedral coordination and are linked in an *anti–syn* arrangement (Barclay & Kennard, 1961). Associated with this linkage is an apparent difference in Zn–O and C–O lengths: mean for Zn–O(1) and Zn–O(2)^{i} of 1·938 (10) Å compared with the mean for Zn–O(3)^{ii} and Zn–O(4) of 1·967 (12) Å, and mean for O(1)–C(1) and O(2)–C(2) of 1·28 (2) Å compared with the mean for O(3)–C(1) and O(4)–C(2) of 1·22 (2) Å, but a comparison with variations in C–C lengths makes it impossible to say that these differences are statistically significant.

References

BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* pp. 3289–3294.

BUKOWSKA-STRZYŻEWSKA, M. (1965). *Acta Cryst.* **19**, 357–362.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.

FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965). *Acta Cryst.* **19**, 548–555.

GHOSE, S. (1964). *Acta Cryst.* **17**, 1051–1057.

GIANCOTTI, V., GIORDANO, F., RANDACCIO, L. & RIPAMONTI, A. (1968). *J. Chem. Soc.* (*A*), pp. 757–763.

HOPPE, W. (1965). *Angew. Chem.* **77**, 484–492.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press.

KIRIYAMA, R., IBAMOTO, H. & MATSUO, K. (1954). *Acta Cryst.* **7**, 482–483.

KROGMAN, K. & MATTES, R. (1963). *Z. Kristallogr.* **118**, 291–302.

LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, p. 291. Copenhagen: Munksgaard.

RAE, A. D. (1975). *Acta Cryst.* **A31**, 575–582.

SIMONOV, YU. A. & MALINOVSKII, T. L. (1970). *Kristallografiya*, **15**, 370–371.

STEPHENSON, N. C., BEALE, J. P. & CRAIG, D. C. (1968). *Natl. Bur. Stand. US, Monogr.* No. 364.

VAN NIEKERK, N. K. & SCHOENING, F. R. L. (1953*a*). *Acta Cryst.* **6**, 609–612.

VAN NIEKERK, N.K. & SCHOENING, F. R. L. (1953*b*). *Acta Cryst.* **6**, 720–723.

VAN NIEKERK, N. K. & SCHOENING, F. R. L. (1953*c*). *Acta Cryst.* **6**, 227–232.

Acta Cryst. (1977). B**33**, 2120–2124

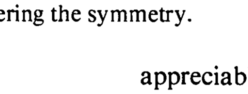
X-ray and Neutron Diffraction Studies of the Hydroquinone Clathrate of Hydrogen Chloride

BY JAN C. A. BOEYENS AND JAN A. PRETORIUS

National Chemical Research Laboratory, PO Box 395, *Pretoria, South Africa*

(*Received* 22 *November* 1976; *accepted* 31 *December* 1976)

The crystals of $C_6H_6O_2.xHCl$, obtained from an ethereal solution of 1,4-dihydroxybenzene saturated with HCl gas, have been examined by X-ray and neutron diffraction: rhombohedral, space group $R3$, with $a(\text{hex}) = 16{\cdot}650\,(1)$, $c = 5{\cdot}453\,(1)$ Å. In two independent analyses the structure was refined to $R(\text{X-ray}) = 0{\cdot}036$ and $R(\text{neutron}) = 0{\cdot}069$. The HCl molecule is oriented within the quinol cavity because of a large number of weak



$$-OH\cdots Cl{-}H\cdots \overset{|}{O}H$$

interactions, which are responsible for lowering the symmetry.

Introduction

The X-ray photoelectron spectrum of HCl, clathrated in a β-quinol framework (Copperthwaite, 1976), differs appreciably from the gas-phase spectrum, suggesting that the structure of the clathrate is not adequately described by the model of Palin & Powell (1947) for the SO_2 clathrate. According to this model the clathrated molecules are rotationally fully disordered in their cavities and show little interaction with the centrosymmetric framework. Since the XPS work indicates a large modification of the valence levels, an ordered arrangement of oriented HCl molecules has been inferred and this implies that crystals of the clathrate should be non-centrosymmetric. To decide whether the XPS shift relates to a change in the H—Cl length the structure of the clathrate has been determined by diffraction methods.

Experimental

Crystals were obtained from a solution of 1,4-dihydroxybenzene in ether saturated with HCl. The mole ratio, $M/3Q = 0{\cdot}87$ established by chemical analysis, corresponds closely to the value given by Palin & Powell (1947). Accurate cell constants were obtained during X-ray data collection. The rhombohedral cell in obverse hexagonal setting was used and the space group was established by structure refinement.

Crystal data

$C_6H_6O_2.\frac{1}{3}HCl$ (ideal composition), rhombohedral, $R3$, $a(\text{hex}) = 16{\cdot}650\,(1)$, $c = 5{\cdot}453\,(1)$ Å, $Z = 9$, $F(000)_X = 540$, $F(000)_N = 41{\cdot}21$, $\mu(\text{Mo } K\alpha) = 2{\cdot}03$ cm^{-1}, $\lambda_N = 1{\cdot}45136$ Å.

The X-ray structure

A unique data set consisting of 313 reflexions above a $3\sigma(F)$ cut-off was obtained on a Philips PW 1100 four-circle diffractometer equipped with a graphite-crystal monochromator. Each reflexion was measured in the ω–2θ scan mode, counting for 20 s over a range of 1° and for the same period on the background. Data reduction consisted of correction for background counts and Lp. The atomic coordinates of the non-hydrogen atoms given by Palin & Powell (1947) for the SO_2 clathrate were used as the trial structure ($R\bar{3}$) and refined by full-matrix least squares. The program *SHELX*-76 (Sheldrick, 1976) was used for all computations. Refinement ceased at $R = 0{\cdot}17$ which suggested $R3$ as the proper space group. Blocked refinement, to avoid correlation problems, of the near-centrosymmetric structure in $R3$ proceeded smoothly to $R < 0{\cdot}1$, at which stage it was possible to locate all but one of the H atoms on a difference map.

Despite the smooth convergence, the final structure showed unrealistic distortions of the hydroquinone molecule. It was further established that these distortions depended on the sequence in which the various atomic positions were refined in the blocked-matrix procedure. The only way in which these problems could be overcome was to refine the phenyl ring as a rigid group with C—C = 1·395 Å and C—C—C = 120°. The H atoms were allowed to refine freely. The convergence was equally good and the anisotropic refinement terminated at 0·036. The site-occupancy factor for Cl was kept at the experimentally determined value of 0·291. To fix the origin the Cl atom was kept at 0,0,0. A common isotropic temperature factor was refined for all the phenyl H atoms.

At convergence, another difference map was examined along 00*z* for any evidence of the H atom of HCl, but nothing conclusive showed up. This prompted the neutron experiment. The final positional parameters are listed in Table 1.* C atoms are numbered cyclically and the OH groups are bonded to the phenyl ring as follows: H(1)–O(1)–C(1), H(4)–O(2)–C(4). The other H atoms have the same numbers as the corresponding ring C atoms.

Table 1. *Final positional* ($\times 10^4$) *parameters with estimated standard deviations in parentheses*

	x	*y*	*z*
(*a*) X-ray analysis			
C(1)	2563 (6)	1320 (6)	3158 (18)
C(2)	2613 (6)	1880 (6)	1195 (18)
C(3)	3360 (6)	2220 (6)	−427 (18)
C(4)	4057 (6)	1998 (6)	−86 (18)
C(5)	4007 (6)	1437 (6)	1876 (18)
C(6)	3260 (6)	1098 (6)	3498 (18)
O(1)	1825 (3)	929 (3)	4701 (12)
O(2)	4766 (4)	2329 (4)	−1787 (12)
Cl	0	0	0
H(1)	1404 (64)	1206 (69)	4963 (234)
H(2)	2074 (50)	1950 (49)	641 (135)
H(3)	3310 (55)	2491 (51)	−1826 (154)
H(4)	5215 (54)	2092 (70)	−1866 (236)
H(5)	4491 (54)	1232 (51)	1980 (153)
H(6)	3215 (49)	696 (51)	5193 (157)
(*b*) Neutron analysis			
C(1)	2538 (6)	1332 (7)	3327 (23)
C(2)	2597 (6)	1890 (7)	1347 (23)
C(3)	3347 (6)	2221 (7)	−261 (23)
C(4)	4039 (6)	1994 (7)	109 (23)
C(5)	3981 (6)	1436 (7)	2088 (23)
C(6)	3230 (6)	1105 (7)	3697 (23)
O(1)	1804 (9)	897 (8)	4700 (32)
O(2)	4733 (12)	2304 (12)	−1855 (33)
Cl	0	0	0
H(1)	1551 (18)	1340 (17)	4513 (48)
H(2)	2016 (20)	2062 (23)	624 (51)
H(3)	3341 (2)	2546 (19)	−2121 (58)
H(4)	5222 (16)	2117 (20)	−1876 (57)
H(5)	4537 (21)	1273 (23)	1941 (51)
H(6)	3152 (21)	593 (20)	4913 (57)
H(7)	0	0	−1946 (317)

---

* Lists of X-ray and neutron structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32420 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The neutron structure

Although single crystals suitable for X-ray analysis are easy to obtain, all attempts to grow them large enough for neutron diffraction produced low-quality crystals. Those which diffracted at acceptable intensity levels were found to give complicated peak profiles. The best available crystal was used and neutron data were collected on the κ–φ diffractometer at the laboratories of the South African Atomic Energy Board at Pelindaba. A pyrolytic graphite monochromator provided a neutron beam $\lambda = 1{\cdot}45136$ Å at a flux of 3×10^6 n cm^{-2} s^{-1}. Peaks were step-scanned in the ω-mode over 2·88°, counting for 16 min per reflexion. 258 measurable reflexions were obtained and after Lorentz correction were used in a full-matrix refinement of the atomic and isotropic thermal parameters from the X-ray study, with scattering lengths from *International Tables for X-ray Crystallography* (1974). Extinction corrections were not applied.

The quality of the data was such that anisotropic refinement of the H atom thermal parameters was not physically meaningful. The same refinement that was done in the X-ray study led to a difference map at $R = 0{\cdot}075$ which showed a broad negative peak representing the H of HCl on the 00z axis. H(7) was placed in this position followed by a final round of least squares which converged to $R = 0{\cdot}069$. The refined parameters are listed in Table 1.

Discussion

The structure is almost centrosymmetric, which complicates the refinement. There are two possible enantiomers which are so alike that any atom can refine into a position characteristic of either enantiomer. Thus there exist a large number of false minima and R is a poor criterion to distinguish between them, since refinement of the thermal parameters can produce equally good mathematical fits for all these arrangements. Refinement of the phenyl C atoms as a rigid body ensures that these atoms, as a group, will take up positions consistent with a single enantiomer. It was argued that this would sufficiently bias the refinement towards this enantiomer that the O and H atoms would avoid the other form altogether. This approach seems to have worked although some of the H atom positions in the X-ray structure could be wrong. The gross features of the two structures are, however, sufficiently alike to indicate that, random errors apart, the same solution has been obtained in the two cases.

A stereoscopic view of the structure is shown in Fig. 1. All the features revealed by the research of Powell and his co-workers, such as the hydrogen-bonded hexagons of O atoms interconnected through the quinol backbones to yield two interpenetrating frameworks, are clearly discernible. Of more relevance in the present context is the shape of the cavity in which the HCl resides and the light it sheds on the interaction between the guest molecule and the cagework.

The structure is non-centrosymmetric since the interaction of the HCl with the host framework is unsymmetrical when sampled along [001]. This is reflected in the arrangement of the –OH groups which form hydrogen-bonded $[\mathrm{OH}]_6$ rings, normal to **c** and one cell translation apart. For a centrosymmetric guest molecule centred at the origin of coordinates the two adjacent $[\mathrm{OH}]_6$ rings should be centred at $0,0,\frac{1}{2}$ and $0,0,-\frac{1}{2}$. A spherically disordered HCl in the cavity should give such an arrangement, with Cl at the centre of the cavity. However, the O atoms occur at $z = 0{\cdot}47$

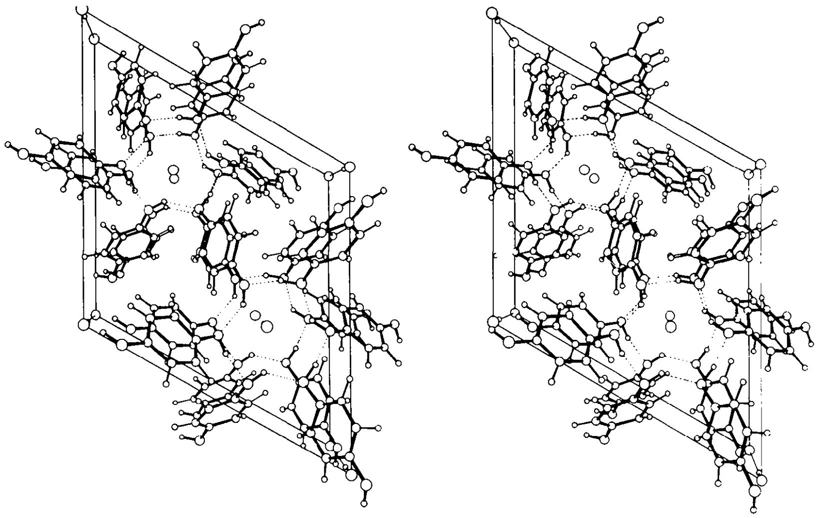
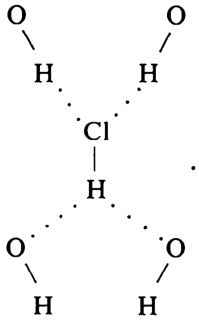


Fig. 1. Stereoscopic drawing of the structure [*ORTEP* (Johnson, 1965)]. Hydrogen bonds in the $[\mathrm{OH}]_6$ rings are stippled in.

and 0·48 (neutron), giving hexagons centred at z = 0·475 and −0·525. The H atom hexagons are centred at 0·465 and −0·535, which means that the OH groups are tilted out of (001) and have their H atoms dipping towards the Cl atom and away from the H on HCl. This implies weak interaction of a type which can be represented schematically as



The shortest contacts in this region are shown in Table 2. The X-ray result is consistent with this, as evidenced by the observed mean O and H z coordinates of 0·48 and 0·43 respectively.

The geometry of the $[OH]_6$ ring is shown in Fig. 2. The X-ray and neutron results are in fair accord. The discrepancy in C—O lengths arises from an oddity in the refinement: although x and y of the C atoms in the rigid phenyl group show excellent agreement for the two data sets z is found to be higher in the neutron case by an average of 0·015 or 0·08 Å. The explanation of this is obscure, but could lie in the quality of the neutron data. It is of more significance that the lengths of 1·38, 1·70, 1·01 and 2·70 Å obtained on averaging over the chemically equivalent separations O—C, O · · · H, O—H and O · · · O are in excellent agreement with the values obtained by Mak, Tse, Tse, Lee & Chong (1976) for the centrosymmetric adduct of H_2S.

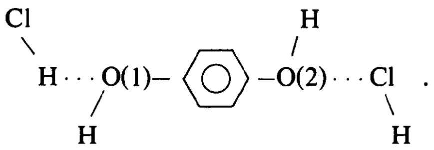
The actual values in the present case show cyclic alternation of shorter and longer O · · · O distances around the $[OH]_6$ ring and this is another manifestation of the guest–host interaction. The two hydroxy ends of each hydroquinone molecule are hydrogen-bonded into different cavity walls and the O · · · O axis of the molecule points at the centres of two different cavities.

Table 2. *Interatomic distances* (Å) *in the clathrate cavity*

H(7) refers to the apparent position of the H on HCl. The values are based on the neutron structure.

O(1)—Cl	3·65 (2)	O(1)—H(7)	3·18
H(1)—Cl	3·46 (3)	H(1)—H(7)	3·10
O(2)—Cl	3·83 (2)	O(2)—H(7)	3·30
H(4)—Cl	3·44 (3)	H(4)—H(7)	2·86

More specifically, the O(2) end points at the Cl and the O(1) end at the H atom of an HCl:



One of these interactions is clearly attractive and the other repulsive. Energy minimization therefore requires some distortion and the result can be seen in Fig. 2.

The position of the H atom of HCl deserves some comment. The apparent bond length of 1·06 Å is obviously too short. The isotropic thermal vibration parameter, $u = 0{\cdot}49$ Å^2, however, indicates either drastic thermal motion or partial disorder. In any event, the HCl molecule seems to lie preferentially on the surface of a cone swept out at an angle of $\cos^{-1}(1{\cdot}06/\sqrt{0{\cdot}49})$ = 33° around 00z and with its apex at the Cl position, giving a bond length of 1·06/cos 33° = 1·27 Å. This corresponds well to the gas-phase value of 1·275 Å (*International Tables for X-ray Crystallography*, 1968).

Conclusion

The non-centrosymmetric space group, the position of Cl in the cavity and the geometry of the $[OH]_6$ rings all indicate some guest–host interaction, as was inferred from the XPS work. The partial disorder of HCl, the comparatively large separation between guest and host atoms and the unperturbed length of the HCl bond, however, show that this interaction is relatively weak and not sufficient to account for the XPS spectrum.

In the recently published structure of the H_2S clath-

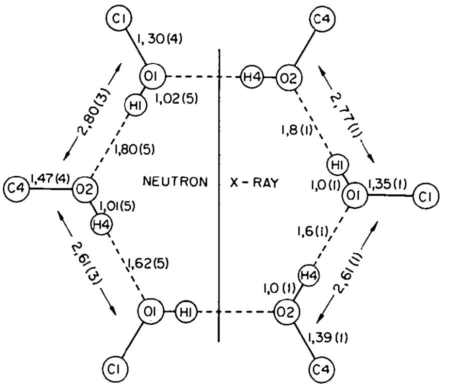


Fig. 2. Schematic drawing to illustrate the geometry of the $[OH]_6$ ring and to compare the X-ray and neutron results.

rate (Mak *et al.*, 1976) the two H atoms of H_2S could not be detected. In the light of the present results it seems reasonable that the H_2S is also rotationally disordered about [001] to lie in the surface of a double cone with S at the common apex. Since H_2S is not linear the cone will be flatter than the HCl cone and, as observed, both the *a* and *c* cell constants should be larger in the H_2S clathrate.

We thank R. G. Copperthwaite for growing the crystals, G. Gafner for assistance with the X-ray data collection and H. W. W. Adrian for operating the neutron diffractometer.

References

COPPERTHWAITE, R. G. (1976). *Chem. Commun.* pp. 707–709.

International Tables for X-ray Crystallography (1968). Vol. III, p. 268. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 270. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAK, T. C. W., TSE, J. S., TSE, C., LEE, K. & CHONG, Y. (1976). *J. Chem. Soc. Perkin* II, pp. 1169–1172.

PALIN, D. W. & POWELL, H. M. (1947). *J. Chem. Soc.* pp. 208–221.

SHELDRICK, G. M. (1976). Private communication.

Acta Cryst. (1977). B33, 2124–2128

Mixed-Ligand Complexes in K_2ReCl_6–K_2ReBr_6 Solid Solution

BY J. HAUCK* AND K. RÖSSLER

Institut für Chemie, Institut 1: *Nuklearchemie, Kernforschungsanlage Jülich GmbH, D*-5170 *Jülich, Germany* (*BRD*)

(*Received* 22 *November* 1976; *accepted* 31 *December* 1976)

K_2ReCl_6 and K_2ReBr_6 form a complete solid solution between 420°C and the melting point at 715–730°C by equilibration with the gas phase. The average Re—*X* length changes continuously from 2·35 Å (K_2ReCl_6) to 2·51 Å (K_2ReBr_6) with a considerable variation of the valence force constant as determined by X-ray diffraction and FIR spectroscopy. The mixed-ligand complexes can be dissolved in aqueous solution and separated chemically. The ligands are distributed randomly, as expected for compounds with weak covalent bonding, with a minimum of short-range order at the 1:1 composition of the solid solution.

Introduction

The crystal structure of coordination compounds in general depends on the type of bonding and the site symmetry of the complexes. Octahedrally coordinated compounds often possess cubic, tetragonal or hexagonal symmetry. If two complexes with different ligands form a solid solution, the symmetry of the complexes and of the crystal structure can change in three different ways: (1) The ligands of the complexes are distributed randomly with a maximum of entropy. All kinds of mixed-ligand complexes coexist without a long-range order. (2) One special configuration of ligands is formed preferentially, but no orientation relative to the other complexes exists. (3) The mixed-ligand complex with one particular configuration has a long-range order, thus forming a superlattice. In this case the solid solution is restricted to certain compositions.

The random orientation of different ligands is often encountered in compounds with ionic bonds such as KCl–KBr solid solution (ss) (Wasastjerna, 1946). With increasing covalency the second and third kind of ordering is preferred. In K_2ReCl_6–K_2ReBr_6 ss, obtained by coprecipitation from aqueous solution, the $ReCl_6$ and $ReBr_6$ octahedra are randomly distributed in the cubic K_2PtCl_6 structure (Müller, 1963). In $K_2[OsO_2Cl_4]$ the anions are ordered in a tetragonally distorted K_2PtCl_6 structure (Kruse, 1961). The third kind of ordering can be determined by X-ray or neutron diffraction. The second possibility can often be studied by spectroscopic methods characterizing the short-range order, such as infrared or electron spectroscopy (e.g. Jørgensen, Preetz & Homborg, 1971). This method, however, becomes more tedious if the solid solution contains several different mixed-ligand complexes with overlapping spectra. Mixed-ligand complexes with very weak covalent bonding, in general, cannot be separated chemically because of ligand exchange.

In the K_2ReCl_6–K_2ReBr_6 system of this in-

---

* Present address: Institut für Festkörperforschung der Kernforschungsanlage Jülich GmbH, Jülich, Germany (BRD).