

## NMR STUDY OF MERCURIC SULFATE MONOHYDRATE

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**T**HE X-ray structural analysis of  $\text{HgSO}_4 \cdot \text{H}_2\text{O}$  was first carried out by Bonefacic.<sup>1</sup> In their refinement of the structure, Templeton *et al.*<sup>2</sup> have commented on the hydrogen bonding in the structure. In view of these comments, it was thought interesting to undertake a PMR study of the single crystal.

$\text{HgSO}_4 \cdot \text{H}_2\text{O}$  belongs to the orthorhombic space group  $\text{Pmcn} - \text{D}_{2h}^{16}$  with four molecules in the unit cell. The general positions are given by:

$$\pm [(x, y, z); (\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z); (\frac{1}{2} + x, \bar{y}, \bar{z}); (\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)]$$

Crystallographically, there are two non-equivalent  $p$ - $p$  vectors in any of the three crystal planes.

Large single crystals were grown in the manner described by Templeton *et al.* They were examined using a modified PKW-type of wide line NMR spectrometer constructed in our laboratory. The signals were recorded for 18 orientations of the magnetic field in the  $ab$ - and the  $bc$ -planes, at intervals of  $10^\circ$  each.

The Pake splitting of the signals due to dipolar interaction,  $\Delta H$  (in gauss) is given by<sup>3</sup>:

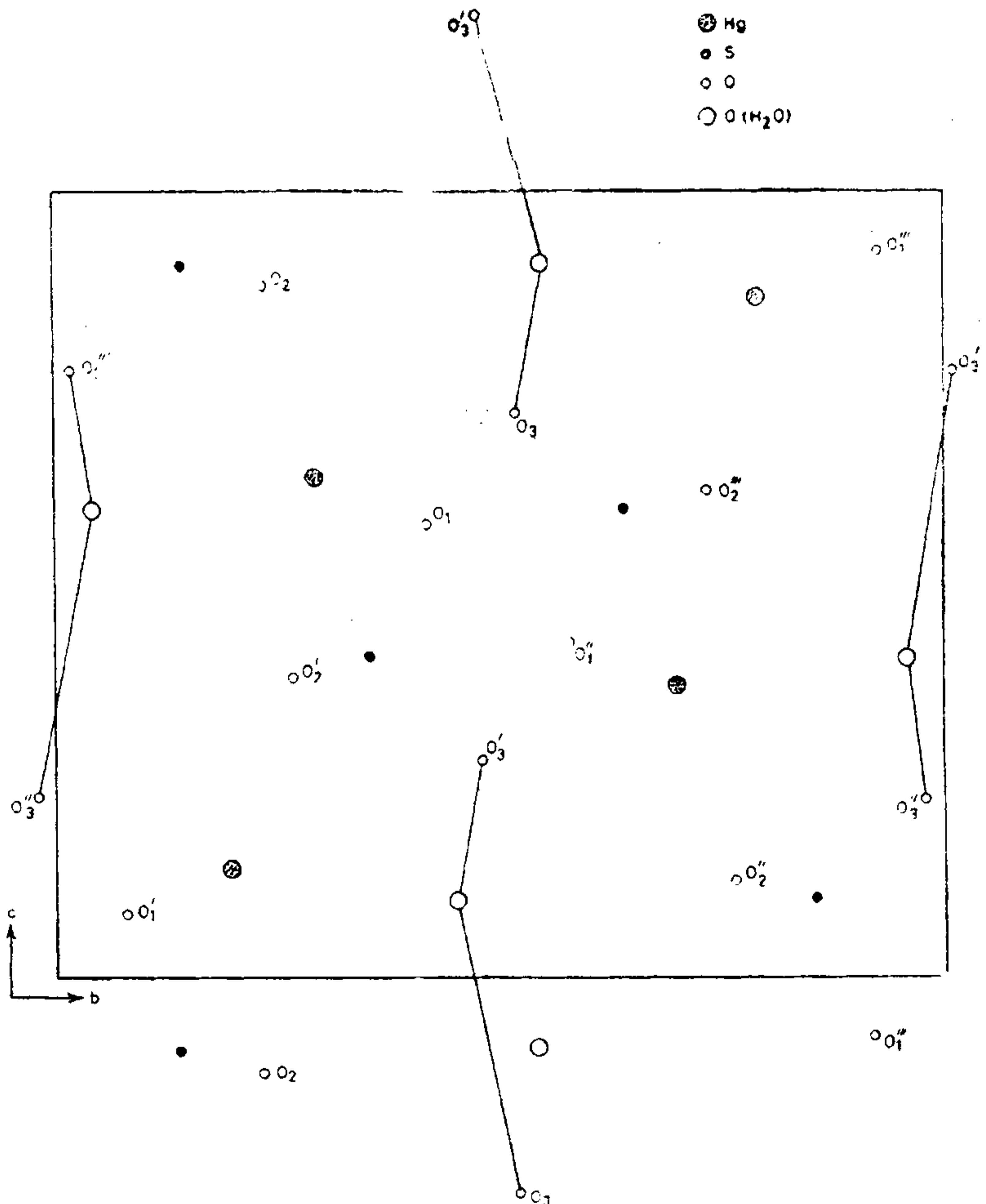
$$\Delta H = 2a (3 \cos^2 \delta \cos^2 \overline{\phi - \phi_0} - 1).$$

The experimental derivative curves for the rotations in the  $ab$ - and the  $bc$ -planes looked similar to the curves usually obtained for a single  $p$ - $p$  vector case. From each of these curves, a small central peak had to be subtracted before further analysis. This peak is presumably due to some free water in the crystal. The curves were resolved into Pake doublet derivatives, with a proper choice of a standard derivative curve from a well-resolved spectrum. The measured  $\Delta H$ -values were then fitted into the Pake equation by the method of least squares. The parameters  $r$ ,  $\phi_0$  and  $\delta$  thus obtained, specify the length and the orientation of the interproton vector with respect to the crystallographic axes.

The interproton distance,  $r$ , was found to be  $1.61 \pm 0.03 \text{ \AA}$

TABLE I

Bond system	Distances in Å	Orientation of $O_A - O_B$ line				Orientation of P-P line				$O_A - O(\hat{H}_2O) - O_B$
		<i>ab</i> -plane		<i>bc</i> -plane		<i>ab</i> -plane		<i>bc</i> -plane		
		$\phi_0$	$\delta$	$\phi_0$	$\delta$	$\phi_0$	$\delta$	$\phi_0$	$\delta$	
$O(3) - O(H_2O) - O'(3)$	2.970, 3.136	$172^\circ 3'$	$57^\circ 51'$	$4^\circ 36'$	$31^\circ 50'$	$175^\circ 63'$	$5^\circ 33'$		$117^\circ 50'$	

FIG. 1. (100) Projection of  $Hg SO_4 \cdot H_2O$ .

For rotation in the *ab*-plane, with the *a*-axis  
as the reference axis,

$$\phi_0 = 175^\circ, \delta = 63^\circ$$

and for rotation in the *bc*-plane with the  
*c*-axis as the reference axis,

$$\phi_0 = 5^\circ, \delta = 33^\circ.$$

Hence, the projections of the p-p vector in the two planes are very nearly parallel to the a- and the c-axes respectively. It is due to this, that we have failed to observe sufficient resolution between the Pake curves corresponding to the two vectors, which are non-equivalent only in respect of their  $\phi_0$ -values. In the ac-plane, however, the spectra observed were typical of two non-equivalent p-p vectors. The parameters are also consistent with the results obtained in the other two planes.

Hydrogen bonding: Each Hg atom in the unit cell has two close neighbours: O(3) at 2.17 Å, and O(H<sub>2</sub>O) at 2.24 Å which are approximately collinear with Hg. The other four neighbours, O(2), are at the corners of a rectangle whose shorter sides are perpendicular to the mirror plane containing Hg, O(3) and O(H<sub>2</sub>O). This mirror is a symmetry requirement of this space group.

Our NMR results are consistent with two possible sets of hydrogen bonds, as follows:

(i) One involving the O(2) atoms not related by the mirror symmetry, and (ii) another involving the O(3) atoms from adjacent unit cells. The scheme (i) however leads to the protons being located along the edges of the

co-ordination polyhedron and this is extremely unlikely.

The distances and angles calculated on the basis of the X-ray data are furnished along with the PMR results, for scheme (ii) in Table I.

The long bond distances involved suggest rather weak bonding; this allows us to assume an O-H distance corresponding to the vapour value, viz., 0.96 Å. This, together with the observed H-H distances of 1.61 Å, gives H-O(H<sub>2</sub>O)-H as 113° 58', which is near the O(3)-O(H<sub>2</sub>O)-O'(3). Hence, we are led to suggest that the bonding to the O(3) atoms of adjacent unit cells is the probable one. The proposed hydrogen bonding is illustrated in Fig. 1.

Such a bonding appears to violate the mirror symmetry of the space group, and a neutron diffraction study of the crystal may be of interest.

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3. Pake, G. E., *Jour. Chem. Phys.*, 1948, **16**, 327