

SHORT COMMUNICATIONS

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On the structure of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ By Z. M. EL SAFFAR, *Department of Physics, De Paul University, Chicago, Illinois 60614, U.S.A.*

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Proton magnetic resonance has been employed to establish the orientations of the water molecules in $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The results are found to be in disagreement with the H-bonding scheme proposed by Grdenić using X-ray diffraction. A rather large proton-proton separation of 1.66 ± 0.01 Å has been determined for the water molecules in this salt both at room temperature and at 77°K.

The angular dependence of the n.m.r. (nuclear magnetic resonance) spectrum from single crystals of mercurous nitrate dihydrate has been studied at room temperature with a view to establishing the orientations of the water molecules. The experimental technique employed and the n.m.r. equipment used have been described elsewhere by the author (El Saffar, 1969). The resonance lines were recorded in two planes of rotation, the (010) plane and a second plane that contains the polar lines 110, 011 and 101. The angular dependence of the line splittings observed in (010) indicates that in this plane all water molecules appear equivalent. The angular dependence of the line splittings observed in the second plane reveals two nonparallel water molecules, one being the mirror image of the other in the (010) plane. The orientation of the second plane of rotation was so chosen that it makes an angle of 5° with one of the two nonparallel p - p (proton-proton) directions. The experimental measurements give a p - p separation of 1.66 ± 0.01 Å and a p - p direction with a polar angle γ of 98° from [001] and an azimuthal angle φ of $\pm 42^\circ$ from [010] in a right-handed coordinate reference. The angular uncertainty involved in locating the p - p direction is estimated to be 3°. The rather large p - p separation was confirmed by further n.m.r. measurements on polycrystalline $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Here the absorption spectrum was recorded at 77°K (to reduce the influence of thermal motion on the shape of the resonance spectrum) and were analyzed by the least-squares method described in detail by Pedersen (1968).

An interpretation of the above results in terms of the available X-ray structure of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is not immediately obvious. The X-ray investigator (Grdenić, 1956) suggested the arrangement $\text{O}(4) \cdots \text{H}-\text{O}(1)-\text{H} \cdots \text{O}(2)$ where O(4) and O(2) are found to be at distances of 2.29 Å and 2.46 Å respectively from O(1), and where the angle $\text{O}(2)-\text{O}(1)-\text{O}(4)$ is 128° . This arrangement gives a hydrogen-hydrogen direction with $\gamma = 129^\circ$ and $\varphi = \pm 84^\circ$ which is in obvious disagreement with the p - p direction determined by n.m.r.

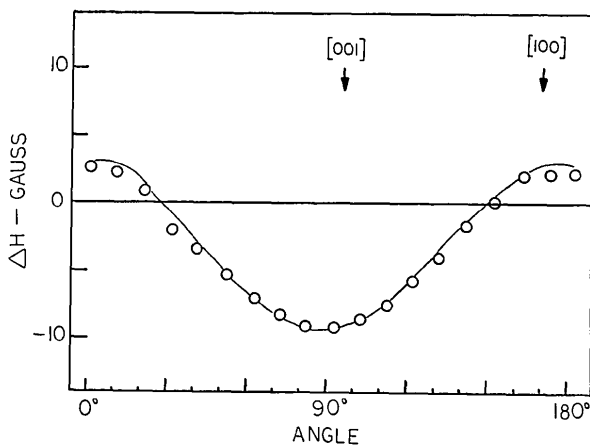


Fig. 1. The proton magnetic resonance line splitting (ΔH) shown as a function of the orientation of the magnetic field in the (010) plane. The minimum in ΔH , which corresponds to an angle of 90° between the magnetic field and the proton-proton vector, yields an accurate value for the proton-proton distance.

In view of the above report and as a result of a close examination of the X-ray structure it appears that at least the oxygen positional coordinates given by Grdenić are in doubt. It is understood that Dr Grdenić and coworkers are presently undertaking a three-dimensional X-ray investigation of this compound (Grdenić, 1973).

References

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