Hydrogen Bond Studies
125. A Deuteron Magnetic Resonance Study of Strontium Formate Dihydrate, $Sr(HCOO)_2 \cdot 2D_2O$

Bo Berglund and Jörgen Tegenfeldt

Institute of Chemistry, University of Uppsala, Sweden

(Z. Naturforsch. **32 a**, 1025–1029 [1977]; received July 22, 1977)

A room temperature (25 °C) deuteron magnetic resonance (DMR) study of a single crystal of $Sr(HCOO)_2 \cdot 2D_2O$ is reported. Signals from all water molecules in the unit cell have been detected, and all four independent electric field gradient (EFG) tensors at the water deuterons have been determined from 409 quadrupole splittings. All spectra were recorded by rotating the crystal about one arbitrarily selected axis. The following quadrupole coupling constants and asymmetry parameters for the deuterons were obtained: 213.5(4), 189.3(4), 195.7(4) and 200.7(5) kHz and 0.117(3), 0.110(4), 0.116(4) and 0.098(3). The directions of the eigenvalues are qualitatively consistent with the crystal structure refined by Galigné [1]; the result is in disagreement, however, with the earlier DMR study of $Sr(DCOO)_2 \cdot 2D_2O$ (Reference [2]).

Introduction

Several papers have been published dealing with the crystal structure of $Sr(HCOO)_2 \cdot 2H_2O$. One structure was suggested by Osaki in 1958 [3] and another by Galigné and Falgueirettes in 1961 [4]. In 1971, Galigné presented a new refinement of the crystal structure using X-ray data [1]; this confirmed the structure proposed by Osaki. The two reports, however, showed some important differences in the interatomic distances.

A deuteron magnetic resonance (DMR) study of deuterated $Sr(HCOO)_2 \cdot 2H_2O$ was undertaken by Dillon and Smith in 1972 [2]; their result was, in part, consistent with the structure proposed by Osaki. In the DMR study, electric field gradient (EFG) tensors were determined for two formate deuterons as well as for two of the crystallographically independent water deuterons.

The crystal structure of $Sr(HCOO)_2 \cdot 2H_2O$ belongs to the orthorhombic space group $P2_12_12_1$ ($a = 7.332$, $b = 12.040$, $c = 7.144$ Å), with four asymmetric units in the unit cell. The structure, shown in Fig. 1, contains two different water molecules (I and II), forming isolated dimers in the structure.

The water molecule II participates in hydrogen bonding to the formate ion, with hydrogen-bond distances 2.736(7)* and 2.715(7) Å. The water molecule I participates in two markedly different hydrogen bonds, one to a formate oxygen with a distance of 2.672(7) Å and one to the oxygen of water molecule I with a distance of 2.808(7) Å [1].

All eight water molecules in the unit cell are magnetically nonequivalent for a general orientation of the crystal relative the magnetic field. Thus, the water molecules will give rise to a total of 16 quadrupole splittings in a DMR experiment for a general rotation axis. As the crystal structure belongs to an orthorhombic space group, the four independent EFG tensors can be evaluated from data obtained by rotating the crystal around only one axis.

It has recently been shown [5] that the quadrupole coupling constants at the deuterium positions in water molecules in solid hydrates are correlated to the stretching frequencies for isotopically dilute HDO molecules. Over the range of frequencies studied, the data were very well described by the linear relation.

$$e^2 q Q/h = 0.173\, \nu_{OD} - 205\,. \qquad (1)$$

During the preparation of this correlation diagram, one of the quadrupole coupling constants previously determined by Dillon and Smith for $Sr(DCOO)_2 \cdot 2D_2O$ (243 kHz) was observed to be about 30 kHz higher than the value predicted from the highest observed stretching frequency for isotopically dilute HDO molecules in $Sr(HCOO)_2 \cdot 2H_2O$ [6]. In view of the otherwise small scatter in the data about the correlation curve, we concluded that at least one of the EFG tensors determined by Dillon and Smith must be incorrect. Furthermore, they could only

Reprint requests to Dr. J. Tegenfeldt, Institute of Chemistry, University of Uppsala, Box 531, *S-751 21 Uppsala*, Schweden.

* Numbers in paranthesis here and throughout this paper are estimated standard deviations in the least significant digits.

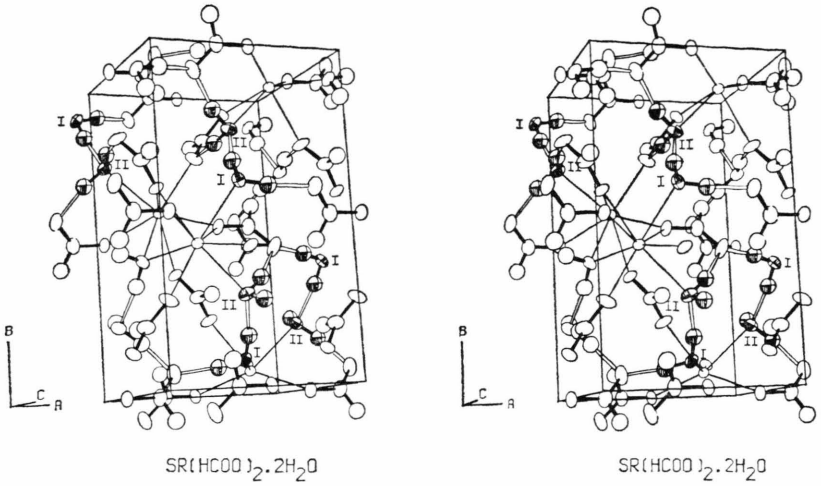

Fig. 1. A stereoscopic illustration of the crystal structure of $Sr(HCOO)_2 \cdot 2\,H_2O$. The eight water molecules which are magnetically non-equivalent with respect to the external magnetic field are shaded. The labels I and II indicate the two crystalographically independent water molecules.

determine two of the four crystallographically independent EFG tensors, as their signal-to-noise ratio was too small. Therefore, we decided to perform a new DMR study on deuterated $Sr(HCOO)_2 \cdot 2\,H_2O$ and, since our primary interest was the quadrupole coupling of the water molecules, we left the formate ion undeuterated. In this way the maximum number of splittings could be reduced from 24 for a fully deuterated crystal to 16.

Experimental

Strontium formate dihydrate, $Sr(HCOO)_2 \cdot 2\,H_2O$, was synthesized from commercially obtained strontium carbonate and formic acid. $Sr(HCOO)_2 \cdot 2\,D_2O$ was prepared by dissolving anhydrous $Sr(HCOO)_2$ in heavy water (99.99% D_2O) and a single crystal of $Sr(HCOO)_2 \cdot 2\,D_2O$ was grown by slow evaporation in a dry atmosphere. After about one week, a large, well shaped crystal was obtained measuring $7 \times 12 \times 18\,mm^3$. The deuterium content in the water molecules was calculated by comparing the O – H and O – D stretching band intensities in an IR-spectrum, and found to be better than 98%.

The single crystal was then mounted on a goniometer head and the rotation axis was chosen to be parallel to a general axis in the crystal in order to avoid unnecessary overlapping of splittings.

The axis of rotation was determined on a 4-circle X-ray diffractometer. The crystal was then transferred to a modified Varian wide-line spectrometer equipped with a 12″ magnet. Deuteron magnetic resonance spectra were recorded at 6.9 MHz by rotating the crystal in steps of 5° through a total of 180°. The precision in the setting of these angles was ±0.05°.

The signal-to-noise ratio was improved by using signal-averaging. About 100 spectra per crystal setting were accumulated in an ALPHA-LSI minicomputer. A typical spectrum is shown in Figure 2.

The magnetic field was swept with a Varian Fieldial unit and the sweep rate was $10\,mT \cdot min^{-1}$. The field sweep was calibrated by recording the positions of the signal from a liquid D_2O sample at various frequencies, measured with a frequency counter. The reproducibility of the sweep rate was 0.1% over the whole period of the data collection. The linearity of the portion of the sweep used was better than 0.3% of the total sweep-width. The RF amplitude was held below saturation level.

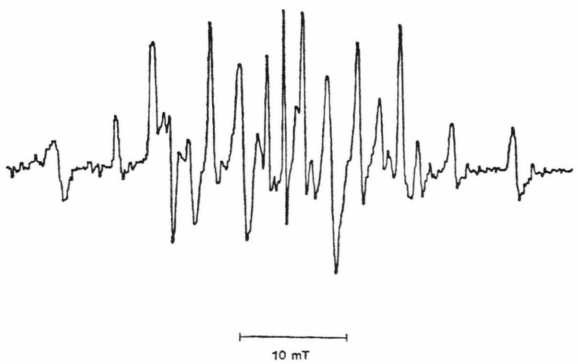

Fig. 2. A typical DMR-spectrum of $Sr(HCOO)_2 \cdot 2\,D_2O$ using signal-averaging.

Refinements

The observed quadrupole splittings were analyzed in a procedure (described briefly in Ref. [7]) using the least-squares program OSPL3 [8]. Preliminary EFG tensors were estimated as follows: quadrupole coupling constants were estimated using the relation (1) between $e^2 q Q/h$ and r_{OD} and the asymmetry parameters were put equal to 0.1. The z-principal axes, corresponding to the largest eigenvalues, were assumed to be parallel to the O – H directions obtained from the structural data [1], and the y-principal axes were assumed to be normal to the water molecule plane. Using these EFG tensors, we generated rotation patterns (16 in all) for the rotation axis, and compared these with the experimental curves. The curves agreed fairly well, and it was possible to assign correctly all the splittings. The preliminary EFG tensors were then used as starting parameters in the program QSPL3. The refinements were based on 527 splittings observed as 409 single or overlapping splittings. A total of 24 parameters were varied; five for each EFG tensor, three for the rotation axis and one for the angle between the axis of rotation and the magnetic field. This angle was not significantly different from 90°. The rotation axis differed by less than 0.1° from that calculated using the X-ray diffractometer. The refined components in the crystallographic system of the rotation axis was 0.0569(2), −0.0233(2) and −0.1210(1). The final root-mean-square deviation between observed and calculated splittings was 4.3 G.

Results and Discussion

The refined EFG tensors are given in Table 1. The rotation patterns based on the parameters after the final least-squares cycle, together with the experimental points are given in Figure 3.

A comparison of the orientations of the EFG tensors in Table 1 with those two given by Dillon and Smith [2] shows that the tensor at deuteron D1 ($e^2 q Q/h = 213$ kHz) corresponds to the symmetry related tensors at D1 and D2 in Ref. [2] ($e^2 q Q/h = 243$ kHz). Furthermore the tensor at deuteron D2 ($e^2 q Q/h = 189$ kHz) corresponds to the symmetry

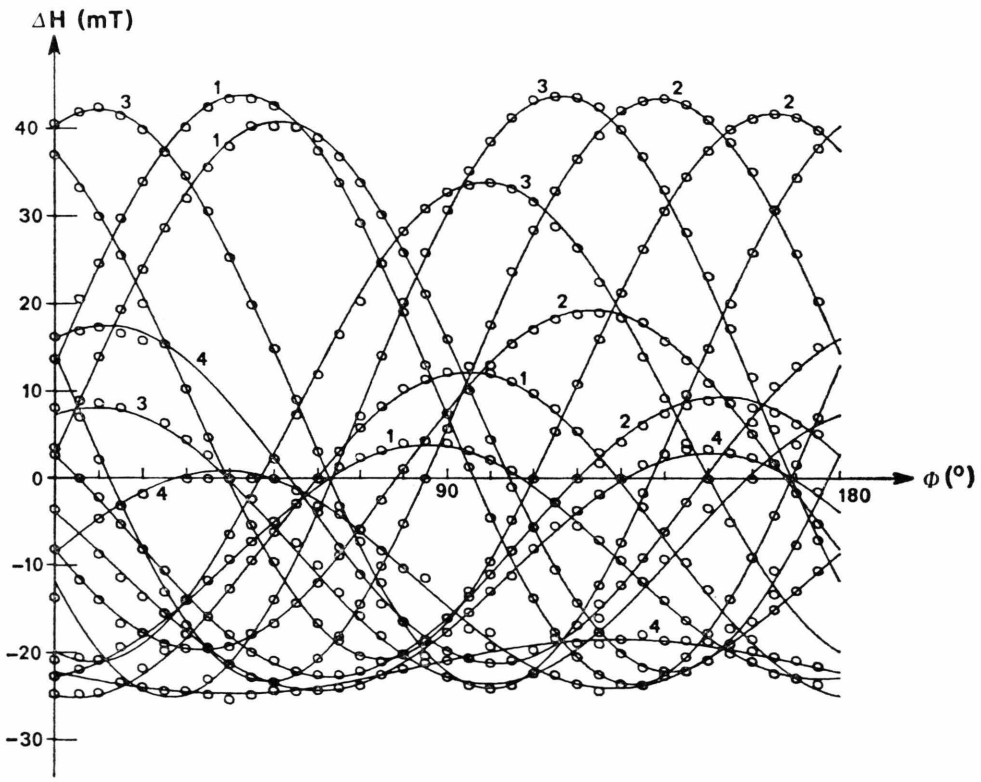

Fig. 3. Rotation patterns based on the parameters given in Table 1. The circles are experimental DMR-splittings. The labels 1–4 correspond to deuteron 1–4.

Deuteron	Eigenvalues (kHz)	Eigenvectors		
D1	− 94.3 (4)	−0.1346 (2)	0.0021 (6)	0.0222 (14)
	−119.2 (4)	−0.0192 (17)	−0.0504 (1)	−0.1095 (3)
	213.5 (4)	0.0104 (1)	−0.0660 (1)	0.0843 (1)
D2	− 84.2 (4)	−0.0535 (2)	0.0558 (10)	0.0880 (16)
	−105.1 (4)	−0.0101 (9)	−0.0585 (9)	0.0988 (14)
	189.3 (4)	0.1251 (1)	0.0191 (1)	0.0456 (2)
D3	− 86.5 (4)	0.0718 (11)	0.0168 (11)	−0.1155 (12)
	−109.2 (4)	0.0603 (13)	0.0635 (3)	0.0657 (21)
	195.7 (4)	0.0990 (1)	−0.0509 (1)	0.0438 (2)
D4	− 90.5 (4)	−0.1141 (10)	0.0455 (10)	−0.0032 (7)
	−110.2 (4)	0.0687 (17)	0.0652 (7)	0.0505 (2)
	200.7 (5)	0.0294 (1)	0.0241 (1)	−0.1305 (1)

Table 1. Eigenvalues and eigenvectors of the EFG tensors at the four deuterons in $Sr(HCOO)_2 \cdot 2\,D_2O$ at 25 °C. The vector components are given in the coordinate system defined by the unit cell axes. The labelling of the deuterons is as in Reference [1].

related tensors at D5 and D6 in Ref. [2] ($e^2 q Q/h = 217$ kHz). It is thus clear that both EFG tensors given by Dillon and Smith are incorrect.

All four quadrupole coupling constants in Table 1 are very close to those predicted from the relation (1). They are also in good agreement with the values expected from a correlation with hydrogen bond distances. For a further discussion of these quantities, see Reference [6].

In Table 2, the four EFG tensors are compared with some crystallographic quantities based on the X-ray data published by Galigné [1]. It is worth noting that the hydrogen positions are determined from X-ray data; they are therefore known to differ systematically from the nuclear positions. The angles in Table 2 involving the hydrogen positions are therefore not as accurate as they would be from neutron diffraction data. The errors in the hydrogen positions are known to have small effects on C – H directions [9], but the error in on O – H direction in a water molecule can be larger. The angle α_2 for the four deuterons are considerably larger than those found in other hydrates as a result of the incorrect hydrogen positions. It has been found in numerous previous cases that the angle α_1 is around one degree, and in several cases it has been found to be zero within experimental errors. It is therefore possible to get a better estimate of the water hydrogen positions in $Sr(HCOO)_2 \cdot 2\,H_2O$ by using the DMR data. By assuming that the z-principal axes are parallel to the O – H directions, and the O – H distances are equal to 0.97 Å, it is possible to estimate the hydrogen positions. These estimated positions are given in Table 3 together with those calculated by Galigné.

Table 2. Some structural quantities related to the EFG tensors at the deuterium nuclei. The angles α_1 and α_2 are between the z-principal axes and the O—H and O···O vectors respectively. The crystallographic data are taken from Reference [1].

Deuteron	O···O (Å)	$e^2 q Q/h$ (kHz)	η	α_1 (°)	α_2 (°)
D1	2.808 (7)	213.5 (4)	0.117 (3)	14.0	5.8
D2	2.672 (7)	189.3 (4)	0.110 (4)	4.7	5.2
D3	2.715 (7)	195.7 (4)	0.116 (4)	3.1	8.0
D4	2.736 (7)	200.7 (5)	0.098 (3)	8.7	8.6

Acknowledgements

The authors wish to thank Prof. Ivar Olovsson for the facilities he has placed at their disposal. This work has been supported by grants from the Swedish Natural Science Research Council which are hereby gratefully acknowledged.

	This work			Galigné		
H1	−0.074	−0.161	0.106	−0.058	−0.141	0.068
H2	0.037	−0.078	−0.020	0.043	−0.071	−0.030
H3	0.112	0.169	0.289	0.107	0.171	0.280
H4	0.045	0.242	0.120	0.052	0.239	0.155

Table 3.
Atomic coordinates for the hydrogen atoms in the water molecules in $Sr(HCOO)_2 \cdot 2\,H_2O$.

[1] J. L. Galigné, Acta Cryst. **B 27,** 2429 [1971].
[2] M. G. C. Dillon and J. A. S. Smith, J. C. S. Faraday Trans. II, **68,** 2183 [1972].
[3] K. Osaki, Ann. Rep. Sci. Works Fac. Sci., Osaka University **6,** 13 [1958].
[4] J. L. Galigné and J. Falgueirettes, C. R. Acad. Sci Paris **253,** 994 [1961].
[5] B. Berglund, J. Lindgren, and J. Tegenfeldt, sub. for publ.
[6] B. Berglund, J. Lindgren, and J. Tegenfeldt, sub. for publ.
[7] B. Berglund, J. Lindgren, and J. Tegenfeldt, J. Mol. Struct **21,** 135 [1974].
[8] J. Tegenfeldt, UUIC-B13-6, Institute of Chemistry, University of Uppsala, Sweden, 1973.
[9] J. Almlöf, Å.Kvick, and J. O. Thomas, J. Chem. Phys. **59,** 3901 [1973].