

## Communications to the Editor

### An X-Ray Diffraction and Infrared-Raman Spectroscopic Study of the Hydrogen Dinitrate Ion, $(\text{O}_2\text{NO}-\text{H}-\text{ONO}_2)^-$ , in Cesium Hydrogen Dinitrate<sup>1</sup>

Sir:

Two very different configurations for the hydrogen dinitrate ion,  $\text{H}(\text{NO}_3)_2^-$ , have been reported in recent x-ray diffraction studies. In the first case<sup>2</sup> of *trans*-[R<sub>h</sub>py<sub>4</sub>-Br<sub>2</sub>]H(NO<sub>3</sub>)<sub>2</sub> four oxygen atoms of two nitrate groups surround a hydrogen atom forming a distorted tetrahedral arrangement in which all O...O separations are long and nearly equal (~3.1 Å). A very different configuration is observed in the second case<sup>3</sup> of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsH(NO<sub>3</sub>)<sub>2</sub> in which two coplanar unidentate nitrate groups are linked by a very short ( $\langle \text{O}\cdots\text{O} \rangle = 2.45$  Å) and apparently linear hydrogen bond. In the latter case the H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> groups are disordered in the crystal. In an attempt to further elucidate the structure of the H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> ion, we have chosen a much simpler system, CsH(NO<sub>3</sub>)<sub>2</sub>, for a combined diffraction and spectroscopic investigation.

Cesium hydrogen dinitrate crystals were grown by evaporation of a saturated CsNO<sub>3</sub>-HNO<sub>3</sub> solution. The compound crystallizes in the orthorhombic space group  $D_{2h}^{24}-Fddd$  with eight formula units in a cell of dimensions  $a = 12.58$  (2),  $b = 7.40$  (1), and  $c = 12.98$  (1) Å. Intensity data were collected on a diffractometer using a balanced-filter peak-height technique (Mo K $\alpha$  radiation). A total of 286 independent reflections were measured to  $2\theta = 50^\circ$  and there was no indication of sample decomposition from reference reflections measured repeatedly. A linear relationship of peak-height to integrated intensity was observed for 40 check reflections out to  $2\theta = 50^\circ$ , and no correction factors were necessary. Each reflection was corrected for absorption ( $\mu_c = 59.8$  cm<sup>-1</sup>). The structure was solved from the Patterson map and refined by a full-matrix least-squares technique to an  $R$  index on  $F_o$  of 0.052. A listing of structure factors and positional and thermal parameters will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material.

The structure is composed of discrete Cs<sup>+</sup> and H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> ions. The cesium ion coordination sphere consists of ten oxygen atoms from surrounding nitrate groups with Cs-O distances ranging from 3.19 to 3.40 Å; the latter distance approaches the sum of the Cs and O van der Waals radii. The most surprising finding is that the H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> ion has four oxygen atoms, from two nitrate groups, arranged in a tetrahedral fashion similar to that reported previously<sup>2</sup> and which is illustrated in Figure 1. The O...O distances in the tetrahedron are long and the nitrate groups are required by symmetry to be planar and crystallographically equivalent. The distances within a nitrate group are N-O (1) = 1.17 (1) Å and N-O (2) = 1.27 (1) Å and the O-N-O bond angles range from 116.7 (1) to 121.6 (1)°. The shortest O...O distance in the anion is rather long (2.86 Å) which suggests that the H-bond between two oxygen atoms is asymmetric. The lack of a mass effect (H vs. D) on the low frequency infrared modes (vide infra) suggests that the proton in the O-H-O bond is in crystallographic disorder. This is consistent with the oxygen atom thermal ellipsoids shown in Figure 1 which are rather prolate suggesting either large-amplitude motion or possible group disorder. From our

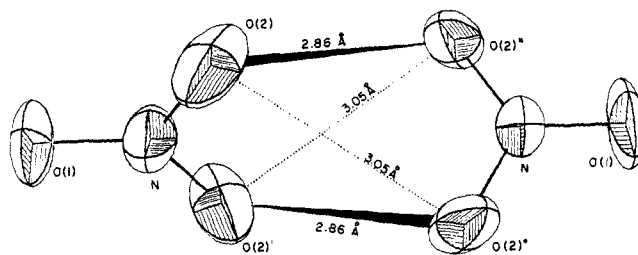


Figure 1. The hydrogen dinitrate ion,  $(\text{O}_2\text{NO}-\text{H}-\text{ONO}_2)^-$ , in CsH(NO<sub>3</sub>)<sub>2</sub> (thermal ellipsoids are scaled to enclose 50% probability). Four oxygen atoms from two nitrate groups form a distorted tetrahedron around a hydrogen atom.

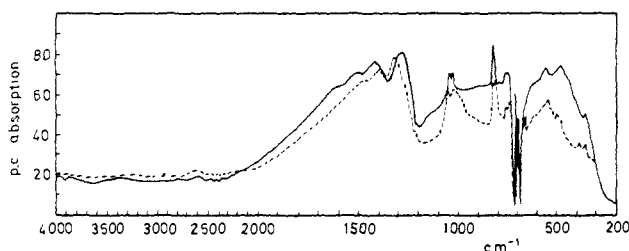


Figure 2. Infrared spectra of CsH(NO<sub>3</sub>)<sub>2</sub> (full treat) and CsD(NO<sub>3</sub>)<sub>2</sub> (dashed) at 90 °K (combined Nujol and Hostafon mulls, PE Mod. 180).

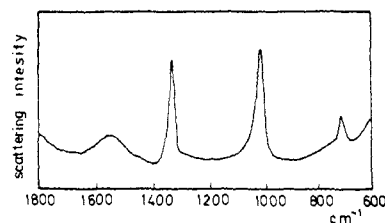


Figure 3. Raman spectrum of CsH(NO<sub>3</sub>)<sub>2</sub> (immersed in CCl<sub>4</sub>, Ar<sup>+</sup> laser excitation).

x-ray difference density maps we cannot locate any residual density which can be attributed to the H atom.

The infrared spectrum of CsH(NO<sub>3</sub>)<sub>2</sub> is presented in Figure 2 and shows no fundamental bands above 2000 cm<sup>-1</sup>. The dominant features are a group of strong and rather broad bands between 1300 and 1600 cm<sup>-1</sup> and an extremely broad absorption culminating near 500 cm<sup>-1</sup> with several peaks superimposed. An Evans type<sup>4</sup> transmission window appears near 700 cm<sup>-1</sup>. The Raman spectrum is given in Figure 3 and shows only a few bands and the broad, low-frequency, infrared feature has no counterpart in it. Deuteration causes the displacement of a component of the group of bands near 1400 to 1010 cm<sup>-1</sup> and only minor changes in frequency of other bands. In particular, the low-frequency, broad feature is not displaced, but is somewhat weakened in intensity. Although, in general, it is easy to sort out the bands due to the skeletal vibrations by considering the Raman spectrum, a detailed assignment of the NO<sub>3</sub><sup>-</sup> bands is not straightforward and will be published elsewhere together with the analysis of some other compounds containing the H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> ion. The deuteration sensitive band near 1400 cm<sup>-1</sup> is likely to be due to an O-H-O deformation mode whereas the broad feature culminating near 500 cm<sup>-1</sup> is tentatively assigned to a protonic

stretching mode. This is done by analogy with the spectra of acid salts of carboxylic acids, and other systems with extremely strong O-H...O hydrogen bonds of which the present one is strongly reminiscent, because of the absence of an OH stretching band above  $2000\text{ cm}^{-1}$  and the appearance of the strong and broad feature at much lower frequencies.<sup>5</sup> The lack of a distinct mass effect on the latter suggests a disordered proton position in the hydrogen bond.<sup>6</sup> The apparently conflicting situation of having a rather long  $R_{O...O}$  but with a spectrum typical of very strong hydrogen bonding may be understood from the ab initio calculation of the potential function of the hydrogen bond in the  $\text{H}(\text{NO}_3)_2^-$  ion.<sup>7</sup> Several other salts of this ion have essentially similar infrared spectra and this is true even of  $\text{Ph}_4\text{PH}(\text{NO}_3)_2$  which seems to contain a much shorter hydrogen bond.<sup>8</sup> In order to locate the H-atom of the  $\text{H}(\text{NO}_3)_2^-$  group, and to further elucidate the nature of the H bonding in  $\text{CsH}(\text{NO}_3)_2$ , we plan to undertake a single-crystal neutron diffraction study.

**Supplementary Material Available:** tables of structure factors and of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) Work performed at Argonne National Laboratory is under the auspices of the U.S. Energy Research and Development Administration. The financial support of the Boris Kidric Fund is acknowledged by R. G., D. H., and B. O.
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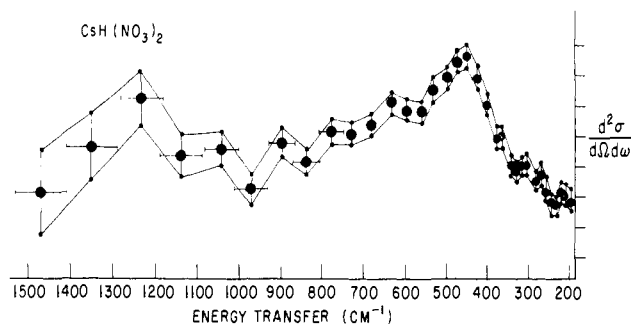
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## Neutron-Scattering Spectrum of Cesium Hydrogen Dinitrate<sup>1</sup>

Sir:

As reported in the previous communication,<sup>2</sup> an x-ray diffraction study of cesium hydrogen dinitrate,  $\text{CsH}(\text{NO}_3)_2$ , has shown that in this compound the two nitrate ions are almost perpendicular, oriented so that four of the oxygen atoms form a distorted tetrahedron. The location of the proton was not obtained in the x-ray study,<sup>2</sup> but the  $\text{NO}_3^-$  groups are presumably held together by a hydrogen bond, and this requires that the proton participate in the tetrahedron. This is an unusual bonding situation, and the dynamics of the proton in this compound are thus of unusual interest. Inelastic neutron scattering is a spectroscopic technique which is especially sensitive to proton motions. Accordingly, we have obtained the neutron-scattering spectrum of cesium hydrogen dinitrate and report the results here.

Approximately 30 g of  $\text{CsH}(\text{NO}_3)_2$  was prepared<sup>3</sup> and



**Figure 1.** Neutron-scattering spectrum of polycrystalline cesium hydrogen dinitrate. The error bars indicate one standard deviation above and below the observed cross section.

loaded into an aluminum cell using a glove box. The cell was sealed and mounted in a cryostat cooled with liquid nitrogen. The spectrum was accumulated over a period of 3 days on a time-of-flight spectrometer installed at the ZING prototype pulsed neutron source at Argonne National Laboratory.<sup>4</sup> The results, corrected for scattering by the cell, are given in Figure 1.

The quantity plotted as intensity is the double differential cross section, which is proportional to the sum (over all nuclei) of the squared vibrational amplitudes weighted by the neutron-scattering cross sections.<sup>5</sup> The cross section for light hydrogen is an order of magnitude larger than for other nuclei in the compound, so major peaks in the spectrum are indicative of large-amplitude vibrations of the hydrogen atom. (Smaller peaks reflect vibrations involving other atoms, sometimes enhanced as the hydrogen is carried along.) The major peaks in the cesium hydrogen dinitrate spectrum are at  $1240 \pm 50$  and  $450 \pm 30\text{ cm}^{-1}$ .

Speakman<sup>6</sup> has designated as type A those acid salts  $\text{MHX}_2$  in which the X groups are symmetrically equivalent. Such salts frequently display very short O...O distances and anomalous infrared spectra. The site symmetry<sup>2</sup> of  $\text{CsH}(\text{NO}_3)_2$  is  $D_2$ , the pairs of oxygen atoms forming the skewed tetrahedron are related by twofold axes, and the substance is therefore type A.

In some type A substances it has been established<sup>7</sup> that the hydrogen bending modes occur at higher frequencies than the stretching modes. For potassium hydrogen bis(trifluoroacetate) this has been confirmed by a neutron diffraction study<sup>8</sup> which shows the thermal ellipsoid for the hydrogen atom elongated in the direction of the bond. Neutron-scattering peaks attributed to hydrogen motion in these compounds<sup>7b,9</sup> are similar to those observed in  $\text{CsH}(\text{NO}_3)_2$ ; hence we believe that the peak at  $\sim 1240\text{ cm}^{-1}$  represents a pair of bending motions and the  $\sim 450\text{ cm}^{-1}$  peak is the stretch. A similar conclusion was reached by Gillard and Ugo<sup>10</sup> in the case of other salts of the hydrogen dinitrate ion.

The position of the proton is not established by either the x-ray diffraction work<sup>2</sup> or the present study; however, the intensity of the satellite peaks at  $\sim 1040$  and  $890\text{ cm}^{-1}$  suggests that the proton is coupled to motions of the  $\text{NO}_3^-$  groups and therefore is not in the center of the tetrahedron. The calculations of Gunde et al.<sup>11</sup> indicate that the position of lowest potential energy for the proton in this system is on an edge of the tetrahedron, midway between the two groups. The x-ray study<sup>2</sup> shows that two such O...O distances are  $2.86\text{ \AA}$  and two are  $3.05\text{ \AA}$ ; it is possible that the proton is positioned on the two shorter edges, implying twofold disorder of either a static or dynamic character. If the disorder were dynamic, broadening of the quasi-elastic peak would be observed. In the present experiment, the width of the quasi-elastic peak (fwhm =  $0.75\text{ meV}$ ) was not perceptibly greater than the instrumental resolution, and we con-