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Crystal Structure of Mercury(II) Hydroxide Nitrate. Refinement by Neutron Diffraction

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The crystal structure of mercury(II) hydroxide nitrate, $Hg(OH)NO_3$, has been reinvestigated by neutron diffraction to obtain information about the hydrogen-bond system. The crystals are monoclinic, space group $P2_1/c$, with $a = 6.57$ (1), $b = 7.19$ (1), $c = 7.83$ (1) Å; $\beta = 115°\ 40\ (10)'$; and $Z = 4$. All atoms were refined with anisotropic thermal parameters. The mercury and oxygen atoms build infinitive zigzag chains with $[Hg(OH)]_n{}^{n+}$ as the structural element where the oxygen atom is three-coordinate and the mercury–oxygen chain is a polymeric oxonium cation. The structural arrangement is such that these chains form quasi layers parallel to (100) with NO_3 ions between them. The mercury atom has two covalent bonds with oxygen atoms inside the chain of lengths 2.079 (5) and 2.093 (5) Å, respectively, and five van der Waals contacts with nitrate oxygen atoms ranging from 2.678 (5) to 2.798 (5) Å. The hydrogen bond (O–H· · ·O) between oxonium and nitrate oxygen atoms is 2.772 (6) Å with an O–H· · ·O angle of 162.8 (6)° and an O–H bond length 0.974 (8) Å.

Introduction

The crystal structure of mercury(II) hydroxide nitrate has already been reported.[2] At that time the structure was solved by the X-ray diffraction method from 570 reflections recorded on equiinclination Weissenberg photographs and measured photometrically. The structures of $Hg(OH)ClO_3$,[3] $Hg(OH)BrO_3$,[3,4] and $Hg(OH)F$,[5] where $[Hg(OH)]_n$ is a structural element which forms an infinite mercury–oxygen zigzag chain, together with the structure of $Hg(OH)_2{\cdot}2HgSO_4{\cdot}H_2O$[6] with a finite (O_3SO)-Hg-(OH)-Hg-(OH)-Hg-(OSO_3) zigzag chain, were also solved by X-ray diffraction. In these structures the hydrogen atom position was not determined. The present paper describes the structure derived by neutron diffraction with coordinates and anisotropic thermal parameters of all atoms.

Experimental Section

Single crystals were prepared as described before.[2] They are monoclinic, with $a = 6.57$ (1), $b = 7.19$ (1), $c = 7.83$ (1) Å; $\beta = 115°$ 40 (10)′; and $d_c = 5.59$, $d_m = 5.47$ g/cm³. The space group is $P2_1/c$ with $Z = 4$. Crystals are stable in air and insoluble in cold water.

The intensities were recorded at room temperature using a manually operated "MAN" diffractometer with a θ–2θ step-scanning technique (at the Institute Boris Kidric, Vinca). The wavelength used was 1.019 Å. About 20 min was spent measuring each reflection. One standard reflection was measured at regular intervals to provide a check on crystal and electronic stabilities. No significant variations were observed. A total of 764 (657 observed) independent reflections were measured from a crystal of volume ≈5 mm³. The intensities were corrected for Lorentz but not for absorption and extinction effects. Signs were attached to observed structure factors using X-ray coordinates,[2] and a three-dimensional Fourier synthesis yielded the position of the hydrogen atom, which was not determined before. The positions of all atoms were then refined by several cycles of full-matrix least-squares refinement, first with isotropic and later with anisotropic thermal parameters. The scattering amplitudes[7] used were $b_{Hg} = 1.27$, $b_O = 0.58$, $b_N = 0.94$, and $b_H = -0.374$, all $\times 10^{-12}$ cm. The weighting scheme adopted was according to the formula already described.[8] The final R value for observed reflections was 0.088 (or 0.102 including unobserved reflections). Calculations were performed on the CAE 90-40 computer using programs written or modified at the Institute Rudjer Boskovic.[9,10]

Description of the Structure and Discussion

Final atomic coordinates and thermal parameters together with their estimated standard deviations are listed in Table I. Standard deviations are about 8 times smaller than those obtained from X-ray diffraction data[2] for all atoms except mercury which has approximately the same standard deviation. Observed and calculated structure factors have been deposited elsewhere.[11] Interatomic distances and angles are given in Table II.

The shortest mercury–oxygen distances, Hg(1)–O(5) of 2.079 (5) Å and Hg(1)–O(5a) of 2.093 (5) Å, belong to a mercury–oxygen infinite chain which is parallel to the b axis (Figure 1). The length of these bonds is similar to that found before[4,5] and differs only slightly from the sum of the covalent radii of mercury[12,13] and oxygen. The angles O(5a)–Hg(1)–O(5) and Hg(1)–O(5)–Hg(1d) are 171.6 (2) and 119.6 (2)°, respectively. The equation of the mean plane through two mercury (Hg(1) and Hg(1a)) and two oxygen atoms (O(5) and O(5a)), together with distances of the atoms from this plane (Table III), indicates that the endless zigzag chain is nearly planar with one mercury atom being 0.035 Å out of the plane. The hydrogen atom is associated with the oxygen atom which belongs to the chain, and the OH group is covalent rather than ionic with an O(5)–H(7e) distance of 0.974 (8) Å. Each oxygen atom in the chain (*e.g.*, O(5)) forms three covalent bonds, two with mercury (*e.g.*, Hg(1) and Hg(1d)) and one with a hydrogen atom (*e.g.*, H(7e)); this bond system is pyramidal (Tables II and III), as was found for the $(OHg_3Cl_3)^+$ ion in the structure of Hg_3OCl_4.[14] The mercury–oxygen chain is a polymeric oxonium ion, $[Hg(OH)]_n{}^{n+}$, as has been found in the structures of $Hg(OH)ClO_3$,[3] $Hg(OH)BrO_3$,[3,4] and $Hg(OH)F$.[5] The structural arrangement is such that the $[Hg(OH)]_n$ chains (designated in Figure 1 by heavy full lines) are parallel with (100) and form quasilayers without direct bond contacts between chains. Nitrate groups are located between those quasilayers and are connected to them by hydrogen bonds. One oxygen atom from the $[Hg(OH)]_n$ chain (*e.g.*, O(5b), Figure 1) and one oxygen from the nitrate group (*e.g.*, O(3), Figure

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Table I. Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Parameters ($\times 10^4$)[a,b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	69 (3)	1312 (3)	2693 (3)	129 (4)	78 (3)	95 (4)	−4 (3)	35 (3)	3 (3)
O(2)	2143 (7)	3964 (7)	5417 (7)	115 (9)	192 (9)	119 (9)	23 (8)	47 (8)	14 (8)
O(3)	4417 (7)	2053 (7)	4966 (8)	101 (9)	120 (8)	163 (9)	−7 (7)	19 (8)	−29 (8)
O(4)	5752 (7)	4235 (7)	7051 (7)	125 (9)	173 (9)	94 (9)	−22 (8)	31 (8)	−34 (7)
O(5)	1058 (7)	−1282 (6)	3957 (6)	114 (9)	79 (7)	110 (8)	−6 (6)	27 (7)	−8 (6)
N(6)	4132 (4)	3410 (4)	5843 (4)	92 (6)	124 (5)	91 (5)	−10 (4)	32 (4)	16 (4)
H(7)	7301 (13)	3656 (13)	500 (13)	180 (23)	145 (16)	175 (19)	−9 (14)	−6 (15)	−43 (14)

[a] The standard deviation of the last significant figure is given in parentheses. [b] Anisotropic thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Interatomic Distances (Å) and Angles (deg) with Standard Deviations in Parentheses[a]

(a) Within $[Hg(OH)]_n$ Chain			
Hg(1)-O(5)	2.079 (5)	O(5)-H(7e)	0.974 (8)
Hg(1)-O(5a)	2.093 (5)		
O(5)-Hg(1)-O(5a)	171.6 (2)	H(7e)-O(5)-Hg(1)	107.9 (4)
Hg(1)-O(5)-Hg(1d)	119.6 (2)	H(7e)-O(5)-Hg(1d)	105.1 (4)
(b) Within Nitrate Group			
N(6)-O(2)	1.265 (5)	N(6)-O(4)	1.228 (5)
N(6)-O(3)	1.253 (6)		
O(2)-N(6)-O(3)	118.9 (4)	O(3)-N(6)-O(4)	120.8 (4)
O(2)-N(6)-O(4)	120.2 (4)		
(c) Others			
O(2)-Hg(1c) O(2g)-Hg(1)	2.678 (5)	O(3)-Hg(1)	2.685 (5)
O(2)-Hg(1)	2.743 (6)	O(4)-Hg(1f) O(4h)-Hg(1)	2.686 (5)
O(2)-Hg(1a) O(2d)-Hg(1)	2.798 (5)	O(3)-O(5b)	2.772 (6)
		O(3)-H(7c)	1.827 (9)
O(3)-H(7c)-O(5b)	162.8 (6)	O(3)-Hg(1)-O(5)	80.7 (2)
O(2)-Hg(1)-O(3)	47.1 (2)	O(3)-Hg(1)-O(5a)	103.6 (2)
O(3)-Hg(1)-O(2g)	75.8 (2)	O(2g)-Hg(1)-O(5)	96.1 (2)
O(2g)-Hg(1)-O(2d)	66.3 (2)	O(2g)-Hg(1)-O(5a)	78.3 (2)
O(2d)-Hg(1)-O(4h)	68.9 (2)	O(2d)-Hg(1)-O(5)	79.1 (2)
O(4h)-Hg(1)-O(2)	112.1 (2)	O(2d)-Hg(1)-O(5a)	92.8 (2)
O(2)-Hg(1)-O(5)	107.8 (2)	O(4h)-Hg(1)-O(5)	92.6 (2)
O(2)-Hg(1)-O(5a)	80.2 (2)	O(4h)-Hg(1)-O(5a)	86.7 (2)

[a] Small letters indicate symmetry transformations and cell translations: (a) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (b) $-x+1, -y, -z+1$; (c) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (d) $-x, \frac{1}{2}+y-1, \frac{1}{2}-z$; (e) $-x+1, \frac{1}{2}+y-1, \frac{1}{2}-z$; (f) $x+1, \frac{1}{2}-y, \frac{1}{2}+z$; (g) $x, \frac{1}{2}-y, \frac{1}{2}+z-1$; (h) $x-1, \frac{1}{2}-y, \frac{1}{2}+z-1$.

Table III. Least-Squares Planes and Deviations of Atoms from the Planes (X, Y, Z Are Fractional Atomic Coordinates)

Atoms and Their Distances (Å) from the Plane

O(5), 0.018; Hg(1), −0.035; O(5a), 0.014; Hg(1a), 0.003
O(2), −0.004; O(3), −0.004; O(4), −0.004; N(6), 0.012
O(5), −0.338; Hg(1), 0.079; Hg(1d), 0.076; H(7e), 0.182
O(2), −0.430; O(3), 0.649; O(2g), −0.505; O(2d), 0.241; O(4h), −0.027; Hg(1), 0.071

Equation of Plane (Fractional Form)

$X/-0.1939 + Y/10.1769 + Z/0.2563 = 1$
$X/-0.4376 + Y/-0.2457 + Z/0.1748 = 1$
$X/-0.3346 + Y/-4.7807 + Z/0.2682 = 1$
$X/0.3002 + Y/-0.0220 + Z/0.0361 = 1$

1) have a separation of 2.772 (6) Å and are involved in a hydrogen bond (designated in Figure 1 by full and broken lines) with an angle at the hydrogen atom, O(3)-H(7c)-O(5b), of 162.8 (6)°. For such an O· · ·O separation in an unsymmetric hydrogen bond, the obtained O-H distance of 0.974 (8) Å is consistent with the curve given by Pimentel and McClellan (Figure 4 therein).[15] In addition to the hydrogen bond, all oxygen atoms of the nitrate groups have contacts with mercury atoms; *e.g.*, O(2) has three contacts with mercury atoms Hg(1c), Hg(1), and Hg(1a) of 2.678 (5), 2.743 (6), and 2.798 (5) Å, respectively; O(3) has contacts with both layers, one through a hydrogen bond and the other, of 2.685 (5) Å, with mercury atom Hg(1); the third nitrate oxygen atom, O(4), has only one contact of 2.686 (5) Å with mercury atom Hg(1f). These contacts are designated in Figure 1 by dotted lines. Nitrate oxygen to mercury atom contacts are slightly shorter than the sum of conventional van der Waals radii[12,13] and are in agreement with observed values for such contacts in other mercury structures containing oxygen.[12,13] Thus each mercury atom exerts two covalent bonds inside the chain and has five van der Waals contacts with neighboring oxygen atoms which belong to nitrate groups. The coordination about the mercury atom is a very distorted pentagonal bipyramid (defined by atoms O(5), O(5a), O(2), O(3), O(2g), O(2d), and O(4h) in Tables II and III). The nitrate group is planar (Table III) with significant differences in N-O bond lengths (Table II), as was found before.[2,16,17] Two bonds are long and do not differ significantly, while the third is shorter. The longest, of 1.265 (5) Å, belongs to oxygen atom O(2) which is directed toward three mercury atoms; the next, of 1.253 (6) Å, belongs to O(3), which is involved in a hydrogen bond and is directed to one mercury atom. The short N-O bond, of length 1.228 (5) Å, belongs to O(4), which is directed to only one mercury atom.

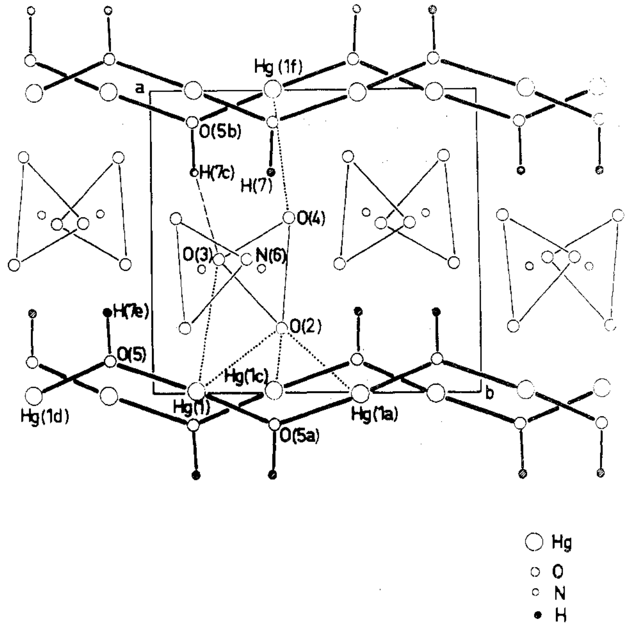

Figure 1. Projection of the structure on (001).

On the basis of the structural results, the compound may

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be expressed in the formula $[Hg(OH)]_n(NO_3)_n$ and described as polymeric mercury(II) oxonium nitrate or as *catena-μ*-hydroxo-mercury(II) nitrate.[18]

Registry No. $Hg(OH)NO_3$, 22640-45-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-3006.

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[18] See nomenclature rules in *J. Amer. Chem. Soc.*, **82**, 5517 (1960).

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Studies of Boranes. XXXVIII. Reactions of Hexaborane(10) with Boron Hydride Lewis Acids[1]

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The reactions of B_6H_{10} with several borane Lewis acids, or their reactive precursors, were studied. The acids B_3H_7 and B_4H_8 react with B_6H_{10} to give *n*-B_9H_{15}. Boron isotopically labeled B_3H_7 and B_9H_{13} react with B_6H_{10} to give *n*-B_9H_{15} and $B_{15}H_{23}$ in which three and nine boron atoms, respectively, are specifically labeled. The acid, B_8H_{12}, reacts with B_6H_{10} to give a new boron hydride, $B_{14}H_{22}$. In the absence of B_6H_{10}, B_8H_{12} is shown to decompose to give $B_{16}H_{20}$ as the only volatile borane. The products of the hexaborane reactions are postulated to arise from a reaction not widely recognized in neutral boron hydride chemistry: the formation of a three-center boron bond by reaction of a hydride containing a B–B two-center bond with an acidic hydride having a readily available empty boron orbital. Reaction mechanism and structures are proposed on the basis of nmr studies.

Introduction

The unstable species BH_3, B_2H_4, B_3H_7, B_4H_8, B_8H_{12}, and B_9H_{13} are all known to form carbon monoxide adducts.[2-7] This property has been cited as evidence for the transitory existence of BH_3[2] and B_4H_8.[8] Extrapolation of this principle supports the contention that these compounds are all capable of a brief existence. For some of these materials other evidence is abundant;[9] indeed, one of them, B_8H_{12}, is an isolable compound.[10] Since many of these acids (if not all of them) appear to be intermediates in boron hydride interconversions, we have attempted to study their reactions with other boron hydrides, at low temperatures, where possible. This article describes our efforts with B_6H_{10} which because of its known Lewis basicity[11,12] seemed particularly likely to react with these species. We have already described the nearly quantitative synthesis of the new hydride $B_{15}H_{23}$ by generation of B_9H_{13} in the presence of B_6H_{10}.[13]

Experimental Section

Methods. The high-vacuum techniques used in this investigation have been described elsewhere.[14,15] Commercially available materials used in this work were purified by standard methods. The 70.6-MHz Fourier transform ^{11}B nmr spectra were obtained with a Varian Associates HR220 spectrometer using a "home-built" pulse apparatus and standard Varian variable-temperature probe accessories. Data manipulation for the instrument was accomplished by means of a Nicolet 1080 computer. Mass spectra were recorded on an AEI Model MS-9 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer.

Preparation of Starting Materials. The compounds B_6H_{10}, B_8H_{12}, and B_8H_{18} were prepared by literature methods.[16-18] Calcium tetrafluoroborate (enriched to 96% ^{10}B by Oak Ridge National Laboratory) was converted to $^{10}B_2H_6$.[19,20] Decaborane(14), enriched to approximately 60% ^{10}B, was prepared by acidification of $KB_{10}H_{13}$ after exchange of this material with $^{10}B_2H_6$.[21] The labeled $B_{10}H_{14}$ was then converted to KB_9H_{14}[22] and to *i*-B_9H_{15} as described previously.[23]

Reactions of Hexaborane(10). Isononaborane(15). Nmr samples of $B_{15}H_{23}$ were prepared by decomposition of *i*-B_9H_{15} of normal and approximately 60% ^{10}B content in B_6H_{10} solution as described previously.[13] Spectra of CH_2Cl_2 solutions of these samples are shown in Figure 1.

Octaborane(12). Due to its extreme instability, B_8H_{12} could be accurately measured only by weight loss from a larger sample at room temperature.[24] Samples of B_8H_{12} (1.82 mmol) and B_6H_{10} (5.47 mmol) were sealed into a break-seal tube (12-mm o.d.) at

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