146 *Inorg. Chem.* **1998,** *37,* 146−148

Isolation of $[Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+}$. Synthesis, ^{9}Be NMR Spectroscopy, and Crystal Structure of $[Be_3(\mu\text{-}OH)_3(H_2O)_6](picrate)_3\cdot 6H_2O$

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Received August 1, 1997

Introduction

Beryllium and its compounds are extremely toxic, but the biological mechanism of their toxicity is still largely speculative. Because of its high stiffness to weight ratio, beryllium is more and more used in several light-weight metal alloys which are indispensable to today's nuclear, aerospace, and electronic industries.[1] Then the concern about the possible pollution by beryllium containing materials is renewing interest in the so far scarcely investigated chemistry of this metal.[2]

The high charge/radius ratio of beryllium makes this element somewhat peculiar with respect to the other elements of group IIA. In particular the beryllium(II) ion shows a strong tendency to form the aquoion $[Be(H_2O)]_4{}^{2+}$, with the water molecules very tightly linked, likely because a significant charge transfer from the water to the beryllium occurs.[3] Recently the structure of the hydrated beryllium and the energetics of the hydration processes have been theoretically investigated.[4] The tetrahedral species $[Be(H_2O)]_4{}^{2+}$, which is stable in acidic aqueous solution, is extensively hydrolyzed at pH > 3. Beryllium hydrolysis has been studied by several authors, and the complex $[Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+}$ has been inferred to be the main species through both potentiometric and NMR measurements.[5] However this trimer, as far as we know, has never been isolated, even if the derivatives $\{Be_3(\mu\text{-}OH)_3(picolinate)_3\}$, $\{Be_3(\mu\text{-}OH)_3(pyrazolylborate)_3\}$, $\{Be_3(\mu\text{-}OH)_3((3,5\text{-}dimethylpyrazolyl)borate)_3\}$, and $[Be_3(\mu\text{-}OH)_3(malonate)_3]^{3-}$ have been structurally characterized.[2d,6,7] We report here the isolation of this trimeric species as the picrate salt $[Be_3(\mu\text{-}OH)_3(H_2O)_6](C_6H_2N_3O_7)_3\cdot 6H_2O$. The compound has been characterized by ^{9}Be NMR and X-ray analysis.

Experimental Section

General Comments. Solvents were reagents grade and were used as received. $Be(OH)_2$ (ICN, Rare&Fine Chemicals) was used as supplied; picric acid (Aldrich) was dried in air, at room temperature. $Be(picrate)_2\cdot 5H_2O$ (**1**),[8a] was prepared according to a previous literature method. ^{9}Be NMR spectra were recorded on a Bruker AC-200 spectrometer, at 28.18 MHz. The measurements were carried out using the axial tube, the inner one containing D_2O to provide a lock signal. The ^{9}Be chemical shifts are reported in parts per million, downfield positive, relative to the external standard 0.1 mol dm^{-1} $Be(SO_4)$ in H_2O.

$[Be_3(\mu\text{-}OH)_3(H_2O)_6](C_6H_2N_3O_7)_3\cdot 6H_2O$ (2). $Be(picrate)_2.5H_2O$ (280 mg, 0.5 mmol) was dissolved in diethyl ether (20 mL) and then benzene (10 mL) was added to the resulting yellow solution. Slow evaporation of the solvent in air, at room temperature, allowed the precipitation of well-shaped, yellow crystals. These were filtered, washed with benzene, and dried in air at room temperature. Yield: 123 mg (75%). Anal. Calcd for $C_{18}H_{33}Be_3N_9O_{36}$: C, 22.09; H, 3.40; N, 12.88; Be, 2.76. Found: C, 22.40; H, 3.20; N, 12.85; Be, 2.70.

Caution! In view of the extreme toxicity of beryllium compounds, all experimental work was carried out in a well-ventilated fume cup board, used exclusively for this work. Spillages must be washed down immediately with water. Established procedures for handling dangerous materials were followed rigorously in all phases of preparation and measurements. Picric acid and picrates are potentially explosive; therefore, these compounds should be handled with great caution.

X-ray Structure Determination of Compound 2. Diffraction data were collected on an Enraf-Nonius CAD4 automatic diffractometer. Unit cell dimensions were determined from the least squares refinement of the angular settings of 25 carefully centered reflections. Crystal data and data collection details are given in Table 1. The intensities were corrected for Lorentz−polarization effects and for absorption.[9] The structure was solved by direct method, SIR92,[10] and refined against all F^2 data by using SHELX93.[11] Only the oxygen atoms were assigned anisotropic thermal parameters.

Results and Discussion

Recently Harrowfield et al.[8] reported that $Be(OH)_2$ reacts with picric acid, in water solution, to give a compound of formula $Be(picrate)_2\cdot 5H_2O$, **1**. The yellow crystals of this complex were unsuited for a structure investigation. We have found that the ^{9}Be NMR spectrum of **1**, in water (0.1 M, pH 3.17), with a sharp signal at 0.07 ppm ($W_{1/2} = 0.8$ Hz) (Figure 1), clearly

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S0020-1669(97)00969-5 CCC: $15.00

Table 1. Crystal Data and Structure Refinement

empirical formula	$C_{18}H_{33}Be_3N_9O_{36}$	dens (calcd)	1.684 g/cm^{-3}
fw	978.56	abs coeff	1.64 cm^{-1}
temp	293(2) K	θ range	2.5−22.5°
wavelength	0.710 70 Å	scan type	$\omega-2\theta$
space group	$P\bar{1}$	scan width	$0.7 + 0.35 \tan \theta$
unit cell dimens		scan speed	1.1−8.24 deg/min
a	11.190(7) Å	refinement method	full-matrix least squares on F^2
b	11.773(1) Å	data/restraints/parameters	5014/0/409
c	15.404(2) Å	goodness-of-fit on F^2	1.020
α	80.08(2)°	final R indices[a]	
β	74.85(3)°	R_1 ($I > 2\sigma(I)$)	0.0684
γ	86.85(2)°	R_{w2} ($I > 2\sigma(I)$)	0.1645
V	1929.4(12) Å^3	R_1 (all data)	0.1378
Z	2		

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{w2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]]^{1/2}$.

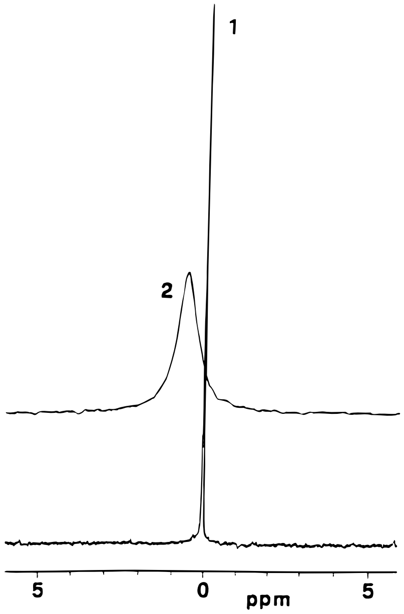

Figure 1. ^{9}Be NMR spectra (H_2O, 293 K) of **1** ($T_c = 0.1$ mol dm^{-3}) and **2** ($T_c = 0.033$ mol dm^{-3}).

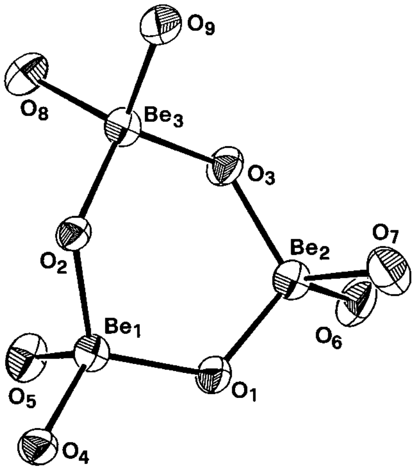

Figure 2. Perspective view of the trimeric species $[Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+}$. ZORTEP[12] drawing with 30% probability ellipsoids. Important bond distances (Å) and angles (deg): Be1−O1, 1.583(8); Be1−O2, 1.601(8); Be1−O4, 1.646(8); Be1−O5, 1.672(8); Be2−O1, 1.580(8); Be2−O3, 1.589(7); Be2−O6, 1.644(8); Be2−O7, 1.660(8); Be3−O2, 1.592(8); Be3−O3, 1.589(7); Be3−O8, 1.666(8); Be3−O9, 1.665(8); O−Be−O 102.8(4)−115.7(5); Be−O−Be 117.5(4)−128.0(4).

indicates the presence of the tetrahedral species $[Be(H_2O)_4]^{2+}$, the picrate ions being then uncoordinated. When compound **1** was dissolved in a diethyl ether/benzene solution, it underwent a hydrolytic reaction which allowed the isolation of well-shaped crystals of composition $[Be_3(OH)_3(H_2O)_6](picrate)_3 \cdot 6H_2O$, **2**. The ^{9}Be NMR spectrum of **2** in water (0.033 M, pH 4.99) (Figure 1) shows a broad resonance at 0.61 ppm ($W_{1/2} = 21$ Hz), likely attributable to the trimeric beryllium(II) hydroxo species.[5b]

The molecular structure of **2** consists of $[Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+}$ cations and picrate anions with water molecules interspersed in the lattice. Figure 2 shows a perspective view of the trimeric cation with important bond distances and angles. The cation can be described as a cyclic structure with a skew-boat[13] conformed, six-membered ring, in which the beryllium atoms are linked by hydroxyl bridges and complete their four coordination through water molecules. The hydroxyl and the water molecules coordinated to the beryllium centers are involved in hydrogen-bonding interactions with the hydroxo− and nitro−oxygen atoms of the picrate anions and with other water molecules present as solvent of crystallization. It ensues a close net of interactions which seems to be the actual stabilizing factor of the tricyclic species $[Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+}$ which was proposed on the basis of the structure of some derivatives (i.e. the picolinate, the pyrazolylborate, and the malonate ones) but never isolated.

The geometry around each metal center is nearly tetrahedral with O−Be−O angles in the range of 102.8(4)−115.7(5)°, the extent of deviation from the limit geometry being rather close to that of the malonate derivative (104.3(7)−113.0(7)°).[2d] A larger distortion has been envisaged in the other $[Be(\mu\text{-}OH)]_3$ rings reported, namely, the picolinate (92.4-116.2°)[6] and the pyrazolylborate ones (99.5−116.0 and 98.7−114.3°),[7] owing to their larger steric demanding. The average values of the Be−O distances, 1.589(3) Å for the inner bonds and 1.659(5) Å for the outer ones, match those reported in the literature.[2d,6,7,14] The O···O contacts, indicative of hydrogen bonding interactions, are numerous and display values in the range 2.6−3.0 Å.

A controlled hydrolysis process, promoted by the dissolution of picric acid in benzene, can account for the formation of the trimeric complex **2**. In the solution of **1** in H_2O the possible equilibrium in Scheme 1 lies quite on the left. The same likely reaction occurs in ether solution. The dissolution of picric acid in benzene likely favors the displacement of the reaction to the

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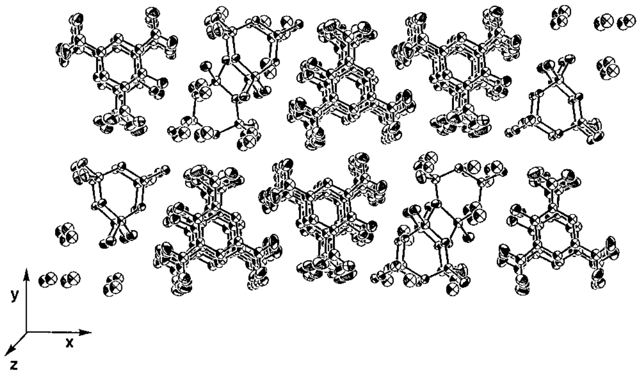

Figure 3. Packing diagram.

Scheme 1

$$3[Be(H_2O)_4]^{2+} + 3(\text{picrate})^{-} \rightleftharpoons [Be_3(\mu\text{-}OH)_3(H_2O)_6]^{3+} + 3H(\text{picrate}) + 3H_2O$$

right; ether evaporation allows the precipitation of the trimeric hydrolyzed species (both complexes **1** and **2** are unsoluble in benzene).

Additional interest in the title compound stems from the presence of the picrate anion. As a matter of fact the structural chemistry of a variety of hydrated metal picrates (IA, IIA, IIIB groups) has been recently reported,[8] characterizing the importance of stacking of the picrate anion as well as its flexibility as a ligand. It is worth noting that the picrate ion acts as a bidentate ligand with small cations as Li^+ and as heptadentate with larger cations as Cs^+ or Rb^+.[8] In the title compound the picrate species, which is essentially planar and packed in parallel stacks (Figure 3 reports the packing diagram), does not bind the beryllium center, not being capable of displacing the water molecules strongly coordinated to the Be(II) ion. In this case the cation works as hydrogen bond donor to connect sheets of stacked picrate entities. This situation is somewhat atypical for the s-block metal picrates, only resembling that found in the magnesium salt.[8] Since the potential chelate ring of the picrate could be most favorable to the small beryllium(II) ion, the actual situation is to be attributed to the large ratio charge/radius of this cation and its large polarizing effect. On going down in the group, as the size of the element increases and the charge transfer to the cation decreases, the binding with the strongly polarizable water molecules becomes less important and the picrate anion becomes competitive.

Acknowledgment. We gratefully acknowledge the financial support of EU for the HCM program “Metals and Environmental Problems” (1995−7), through Grant ERBCHRX-CT94-0632.

Supporting Information Available: Tables listing crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

IC970969X