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ICA Review

Chemistry of Beryllium μ_4-Oxoacetato Complexes

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CONTENTS

1. Introduction

The paper represents a review of the existing data on the synthesis, properties, and structures of beryllium acetato complexes containing four-coordinate oxygen atoms, including the widely known basic beryllium acetate, $Be_4O(OOCCH_3)_6$, along with recently reported beryllium oxomonohydroxo(alkoxo)penta-acetate, beryllium dioxodihydroxooctaacetate, berlylium dioxooctaacetate and its amine and ammonia derivatives, and beryllium dioxohexaacetate. Most complexes are volatile and highly soluble in non-polar media. The properties of beryllium μ_4-oxo derivatives are discussed in terms of the nature of the Be–O bonds and stereochemical considerations.

Unique features of beryllium complexes with organic ligands depend to a great extent on the fact that beryllium, though a typical metal, has an exceedingly small ionic radius. Compact inorganic skeletons are effectively screened by outer organic groups in such complexes, which makes them similar to organic compounds. Low molecular weight beryllium complexes (basic acetate, β-diketonates, *etc.*) have low melting points, are volatile, and easily soluble in organic solvents.

Like most metals beryllium shows no tendency for multiple bonding, and as a rule it forms tetrahedrally coordinated species utilizing its sp^3 orbitals in the condensed phases, with very few exceptions where the tetrahedral coordination cannot be realized because of steric limitations. As a consequence, the acetato group mostly functions as a bidentate ligand in binding with beryllium, as this is usually the case with metal acetates. However, cyclic structures can hardly occur in beryllium acetato complexes because of a small ionic radius of the metal. Therefore structures with bridging acetato groups are formed to yield polymeric or oligomeric species. For a long time, basic beryllium acetate, $Be_4O(OOCCH_3)_6$ and its carboxylate analogs have been the only low molecular weight compounds of this type known. In recent years, however, other oligomeric beryllium acetato complexes have been isolated which possess properties even more interesting than those characteristic of basic carboxylates.

2. Basic Beryllium Acetate

μ_4-Oxohexa-μ-acetatotetraberyllium (basic beryllium acetate) appears to be the most stable beryllium acetato complex. It is readily formed in acid media (by treating beryllium hydroxide[1] or subcarbonate[2] with acetic acid) and as the final product of thermal decomposition of other beryllium acetato derivatives.

The structure of this compound has received a great deal of attention[3–9]. Three crystal modifications of basic beryllium acetate are known, of which the cubic one (T_h^4, a = 15.74 Å, Z = 4) is stable at room temperature and that with a monoclinic lattice (a = 13.60, b = 9.24, c = 16.20 Å, β = 98°, Z = 4) can exist at room temperature indefinitely. Table I gives bond lengths and valence angles of the molecule as obtained from structure studies of the cubic form.

TABLE I. Bond Lengths and Valence Angles of the $Be_4O(OOCCH_3)_6$ Molecule[8].

Bond lengths, Å		Valence angles,	°
C–C	1.500	OCO	123.4
C–O	1.264	$O_{cent.}BeO_{carb.}$	115.2
$Be–O_{cent.}$	1.666	$O_{carb.}BeO_{carb.}$	102.7
$Be–O_{carb.}$	1.624		
C–H	1.1		

The OBe_4 tetrahedron is the basic feature of the structure (Figure 1). Each of the Be atoms is linked with the other three ones through the central oxygen atom and bridging acetato groups so that 6 six-membered cycles occur in the molecule. These are nearly

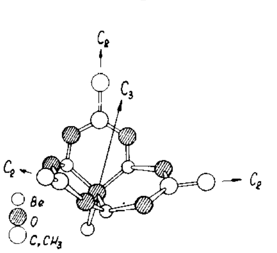
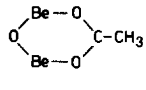


Figure 1. Molecular structure of $Be_4O(OOCCH_3)_6$ (a fragment).



planar, but not strictly so, because of a slight torsion around the C_2 axes. As a result, the molecular symmetry is T rather than T_d, but this departure from the tetrahedral symmetry can often be neglected.

The compact inorganic skeleton of the molecule is fully screened by the outer organic groups which explains the low melting (284 °C) and boiling (331 °C) points and the high solubility of the compound in organic solvents (chloroform, carbon tetrachloride, benzene).

The vibrational spectra of basic beryllium acetate could have been interpreted thanks to its rather high molecular symmetry. Funck[10] made the start on this problem by analyzing the IR spectrum of the basic acetate in the region of 700 to 4000 cm^{-1} in terms of characteristic vibrations of the acetato ligand and the BeO_4 tetrahedron. Later[11], we considered the problem in more detail on the basis of comparative studies of the IR and Raman spectra of basic beryllium formate, acetate and some other beryllium acetato complexes. The data obtained allowed a full assignment of the bands observed in the range 100 to 4000 cm^{-1} in terms of symmetry types and (tentatively) internal coordinates.

Collating the spectra of related compounds reveals that the bands observed above 800 cm^{-1} are, in general, characteristic of the ligands, whereas the bands in the range 400 to 800 cm^{-1} arise from strongly mixed vibrations involving both the beryllium–oxygen skeleton and the organic part of the molecule, so that the spectra of the acetato complexes are very different from that of basic beryllium formate in this region. Still lower frequency bands are characteristic of the inorganic skeleton involved: the low-frequency spectra of basic beryllium acetate and formate are closely similar and markedly change on going to compounds containing modified beryllium–oxygen skeletons.

As mentioned, basic beryllium acetate is exceedingly stable. However, it decomposes under the action of strong bases which can form hydrogen bonds (ammonia and primary amines), reactive acylating agents like acetyl chloride, and also on refluxing with water and alcohols. All these reactions give the products that readily undergo thermolysis to recover the initial basic acetate (or its structure analogs). On the other hand, reactions are known in which the inorganic skeleton of basic beryllium acetate remains intact. Below, we shall first discuss reactions of the latter type.

A. Exchange Reactions

A partial or full substitution of the acetato groups of basic beryllium acetate occurs when the latter is fused together with its carboxylate analogs (basic monochloroacetate[12], basic proprionate[13]) or treated with carboxylic acids, pure or in solution (proprionic[13], monohaloacetic[14], benzoic[14]). Similar products were claimed to occur in the reaction of basic beryllium propionate with acetyl chloride[13].

The results obtained by Wynne and Bauder[15] in their NMR study of the exchange between basic beryllium acetate and trichloroacetate in chloroform solution are very important. These authors have shown that the first formed products contain the ligands in a 5 : 1 ratio. The 5 : 1 species convert partially to $Be_4O(OOCCH_3)_3(OOCCCl_3)_3$ with time, and the equilibrium is attained rather slowly. The mass spectral data (see below) also point to remarkable stability of the $Be_4O(OOCCH_3)_5^+$ unit.

Rather low rates of the exchange processes involving beryllium basic acetate indicate that the compound is hardly ionized in melts and solutions. Stability of the $Be_4O(OOCCH_3)_5^+$ group will be discussed in Section 3.A. on the basis of stereochemistry considerations.

B. Addition Reactions

The interaction of basic beryllium acetate with pyridine and dioxan had been considered an addition reaction for a long time[16–18]; later, the reaction was shown to require the presence of water and to result in destruction of the beryllium–oxygen frame[19] (see 2.C). Likewise erroneously were interpreted the reactions with ammonia and primary amines.

At present, only two addition reactions involving basic beryllium acetate are known: those with SO_2 and with N_2O_4.[20,21] Vapour pressure studies of the corresponding equilibria suggest the following reaction schemes:

$$Be_4O(OOCCH_3)_6 + 2SO_2 = Be_4O(OOCCH_3)_6 \cdot 2SO_2 + 18.5 \text{ Kcal}$$

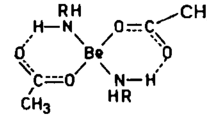
$$Be_4O(OOCCH_3)_6 + 1.5N_2O_4 = Be_4O(OOCCH_3)_6 \cdot 1.5N_2O_4 + 20.2 \text{ Kcal}$$

The adducts are unstable and readily decompose to the components at ambient temperature (via the formation of the 1 : 1 intermediate in the case of SO_2). The adduct with SO_2 crystallizes in the cubic lattice of basic beryllium acetate with a somewhat greater parameter. This fact as well as the low heats of formation of the adducts suggest that the dioxide molecules are physically incorporated in the lattice of the host compound. Presumably, they occupy cavities formed by three adjacent 6-membered cycles like that shown in Figure 1. The low-temperature Raman spectra[22] show that the vibrational parameters of the entrapped dioxide molecules are practically the same as those characteristic of the free molecules in the condensed phase. The spectra provide a convincing evidence for the presence of the dimeric N_2O_4 molecules in the corresponding adduct, in agreement with earlier magnetic studies.

C. Decomposition Reactions

The action of acetyl chloride on a refluxing solution of basic beryllium acetate in acetic acid[23] as well as heating basic beryllium acetate with a mixture of acetic acid and acetic anhydride in an ampule[16] lead to acylation of the compound resulting in the formation of beryllium acetate, $Be(OOCCH_3)_2$. The products from both preparative methods give the same powder patterns but somewhat differ in their IR spectra in the region of the CO stretching vibrations. However, their low-frequency spectra are practically identical and agree well with what can be expected for compounds containing slightly distorted BeO_4 units with the C_{3v} symmetry[24].

We believe that both forms of beryllium acetate are spatial polymers. This conclusion is based on their physical properties, vibrational spectra, and geometrical considerations. $Be(OOCCH_3)_2$ is insoluble in inert solvents, but readily dissolves in liquid ammonia and primary amines to yield, after removal of excess solvent, crystalline products of the composition $Be(OOCCH_3)_2 \cdot 2RNH_2$, where R stands for H, CH_3, C_2H_5, or C_3H_7[25,26]. The products are mononuclear complexes with mixed ligands containing BeO_2N_2 units with the C_{2v} symmetry, as evidenced by their IR and Raman spectra[26]. Stability of such compounds can be attributed to the formation of intramolecular hydrogen bonds incorporated in the 6-membered cycles of the type:



The fact that tertiary amines do not react with beryllium acetate lends support to this conclusion. The acetato group C–C stretches appear at 940 to 955 cm^{-1} as the only strong band in the Raman spectra of the complexes in this region, which indicates the presence of monodentate acetato ligands and thus favours the proposed structure (bidentate acetato groups give the corresponding bands at 970 to 990 cm^{-1} in beryllium complexes). Nevertheless, according to the IR data, the two CO bonds of the ligand remain essentially equivalent in these compounds, thanks perhaps to hydrogen bonding and charge redistribution over the "chelate" cycle.

Thermolysis of beryllium acetate (150 to 200° C) and its amine derivatives (120° C) leads to the formation of basic beryllium acetate.

The first study of the interaction of basic beryllium acetate with ammonia was carried out with chloroform solutions[27]:

$$Be_4O(OOCCH_3)_6 \xrightarrow[CHCl_3]{NH_3} Be_4O(OOCCH_3)_6 \cdot NH_3 \xrightarrow[CHCl_3]{NH_3} Be_4O(OOCCH_3)_6 \cdot 3NH_3 \rightarrow \text{compound III} + \text{compound IV}$$

However, the isolation of solvent-free intermediates was not achieved. The final products contained Be and the acetato groups in 1 : 2 and 3 : 4 ratios, respectively. No definite results were obtained, probably because of complications due to side reactions involving the solvent.[28]

Pure ligands react with basic beryllium acetate in a much simpler way:

$$Be_4O(OOCCH_3)_6 + (n+2)RNH_2 = Be_3O(OOCCH_3)_4 \cdot nRNH_2 + Be(OOCCH_3)_2 \cdot 2RNH_2,$$

where n = 2 (R = CH_3) or 3 (R = C_2H_5, C_3H_7, C_4H_9)[29]. The first product precipitates soon after dissolving basic beryllium acetate in a water-free amine, while the second one remains in the solution. The precipitates readily lose one of the amine molecules to yield $Be_3O(OOCCH_3)_4 \cdot 2RNH_2$ which can be used as starting material for the synthesis of a number of compounds of the μ_4-oxoacetato series (see below).

Alcohols do not react with basic beryllium acetate in the cold. Refluxing the basic acetate with lower primary alcohols (up to butanol) leads to its decomposition and to the formation of voluminous precipitates, practically insoluble in alcohols, of the composition Be(OOCCH$_3$)(OR).[31] The products were shown to contain no unreacted alcohol[31,32]. Nearly at the same time, the reaction was studied by Hardt[33–35] who erroneously treated the products as solvates of basic beryllium acetates other than the initial Be$_4$O (OOCCH$_3$)$_6$.

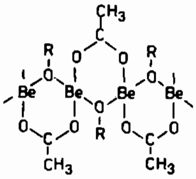
Debye photographs of beryllium alkoxoacetates show them to be amorphous powders. The alkoxo derivatives are insoluble in alcohols but dissolve, after swelling, in chloroform and acetonitrile. Molecular weights of some of the products are given in Table II.

TABLE II. Molecular Weights (M$_0$) of Be(OOCCH$_3$)(OR) in Chloroform Solution and Numbers of Formula Units per Molecule (n)[36–38].

Compound	Be(OC$_2$H$_5$)(OAc)[a]			Be(OC$_3$H$_7$)(OAc)	Be(OC$_4$H$_9$)(OAc)
M$_0$	2000	2500	5670	5400	5700
n	18	22	50	40	40

[a] The three sets of data are given for the products obtained from 99, 99.5, and ≈ 100% ethanol, in the order of increasing M$_0$ values.

The IR spectra of beryllium alkoxoacetates can be interpreted in terms of vibrations of bridging acetato groups, bridging alkoxy groups and distorted BeO$_4$ tetrahedra. Since, according to other evidence, the products represent linear polymers, the following structure can be written[38]:



The presence of 6-membered cycles and the screening effect of the alkyl radicals seem to be responsible for the rather low reactivity of these compounds: alkoxoacetates do not interact with ammonia and amines and are relatively stable towards the action of water. The reaction with water leads to partial substitution of the ligands with the hydroxy groups which seems to have no pronounced effect on the chain structure, although it considerably increases the solubility of the products in alcohols. It should be noted that hydrolysis of alkoxoacetates is an essentially reversible process.

Water reacts with basic beryllium acetate at a rather slow rate and via the formation of a number of intermediate products. Tanatar[2] claims an amorphous product of the composition Be(OH)(OOCCH$_3$)·Be(OOCCH$_3$)$_2$ to be formed when refluxing basic beryllium acetate with water. Quenet[30] has studied the processes that occur in aqueous suspension of basic beryllium acetate at 20° C to show that Be$_4$O$_3$ (OOCCH$_3$)$_2$ is eventually formed. However, no evidence has been presented which would allow to treat such products as individual chemical compounds.

The hydrolysis with water in pyridine or dioxan solutions goes much easier and always to the same effect[19], presumably because of hydrogen bond stabilization of particular products:

$$Be_4O(OOCCH_3)_6 + 3H_2O + 4C_5H_5N = 4Be(OH)(OOCCH_3)\cdot C_5H_5N + 2CH_3COOH$$

$$Be_4O(OOCCH_3)_6 + 3H_2O + 2C_4H_8O_2 = 4Be(OH)(OOCCH_3)\cdot 0.5C_4H_8O_2 + 2CH_3COOH$$

One can easily remove the solvent molecules from both products (60 to 70° C, 0.1 mm Hg)[19,39] to obtain beryllium hydroxoacetate, Be(OH)(OOCCH$_3$). The latter exhibits the OH stretching vibrations at 56 and 268 cm^{-1} higher frequency than the dioxan and pyridine adducts, respectively, which indicates that the adducts comprise rather strong hydrogen bonds of the type OH···base. The formation of such bonds seems to determine the adduct composition: 1:1 or 2:1 adducts are formed depending on the number of atoms capable of hydrogen bonding in the base molecule.

Beryllium hydroxoacetate closely resembles its alkoxo analogs, in particular, in the character of its IR spectrum (Table III). Obviously, these compounds

TABLE III. The Main Frequencies in the Spectra of Be(OC$_2$H$_5$)(OOCCH$_3$) and Be(OH)(OOCCH$_3$) (cm^{-1}).

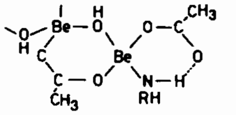
Compound	ν_{as}(CO)	ν_s(CO)	ν(CC)$_{OAc}$	ν(BeO)	δ(BeO$_4$)
Be(OC$_2$H$_5$)(OOCCH$_3$)	1572	1466	967	770	366
Be(OH)(OOCCH$_3$)	1573	1470	970	785	365

have similar structures. However, unlike the alkoxo derivatives, beryllium hydroxoacetate is rather reactive. It readily dissolves in alcohols and can exchange its hydroxy groups for alkoxy ones[39]:

$$Be(OH)(OOCCH_3) + C_2H_5OH \rightleftarrows Be(OC_2H_5)(OOCCH_3) + H_2O$$

The equilibrium is strongly on the side of insoluble alkoxoacetates so that the exchange proceeds to fully substituted products.

In addition to the mentioned adducts with pyridine and dioxan, beryllium hydroxoacetate forms complex compounds with ammonia and primary amines[40] of the composition $Be(OH)(OOCCH_3)\cdot 0.5RNH_2$ ($R = H, C_3H_7$), presumably with polymer or trimer structure. The latter should contain fragments of the type:



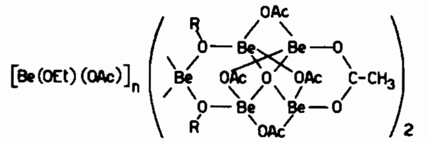
The Raman spectra indicate the presence of both mono- and bidentate acetato groups in the amine complexes of beryllium hydroxoacetate and thus favour the low-molecular weight model.

3. Monosubstituted Beryllium μ_4-Oxopenta-μ-acetato Complexes

A. μ_4-Oxomono-μ-alkoxopenta-μ-acetatotetraberyllium

Vacuum thermolysis of beryllium alkoxoacetates ($p \approx 1 \times 10^{-2}$ mm Hg, $t = 100$–$200\,^\circ C$) leads to the formation of sublimates of the composition $Be_4O(OOCCH_3)_5OR$ ($R = CH_3, C_2H_5, C_3H_7$)[41,42]. The solubility of the products in organic solvents (chloroform, benzene, carbon tetrachloride) exceeds that of basic beryllium acetate. In addition, they are markedly soluble in n-hydrocarbons, especially at elevated temperatures. Purification of the ethoxo derivative by Soxhlet extraction with n-pentane yields the product with a m.p. of 223° C which sublimes at temperatures about 60° C lower than basic beryllium acetate. The molecular weight determinations in benzene and chloroform solutions give values corresponding to one formula unit.

The yield of the product depends strongly on the water content in the alcohol used for the synthesis of the initial beryllium ethoxoacetate[36]. The products obtained in the presence of water consist of shorter chains than those prepared under water-free conditions (see Table II). It has been shown that one polymer molecule yields two molecules of the oxomonoethoxo derivative under the thermolysis conditions. It is likely, therefore, that the decomposition occurs at the chain terminals, whereas the chains proper remain intact in the thermolysis as evidenced by the IR spectra of the residual unsublimable products. These are practically identical with the spectra of beryllium alkoxoacetates obtained in the reaction with "absolute" alcohol. We suggest that the alkoxoacetate chains contain μ_4-oxo units at their terminals[36]:



Cleavage of such terminal groups may be associated with the building up of longer chains or cyclic polymer structures.

The composition and properties of oxomonoalkoxo derivatives point unambiguously to their structure similarity to basic beryllium acetate. This conclusion finds a supporting evidence in the fact that lattice dimensions of monoclinic structure modifications of both compounds differ insignificantly ($Be_4O(OOCCH_3)_5OC_2H_5$: a = 14.79, b = 9.11, c = 16.68 Å, β = 112° 24′, Z = 4; *cf.* the data cited on p. 269)[43]. The structure shown in Figure 2 is quite consistent

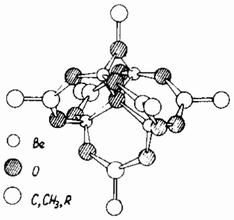
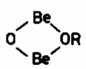


Figure 2. Molecular structure of $Be_4O(OOCCH_3)_5OR$.

with spectral data. Firstly, the vibrational spectra show the molecule to contain the BeO_4 and OBe_4 tetrahedra as well as the bridging acetato groups. On the other hand, the NMR spectrum reveals the presence of two types of acetato groups in the ratio of 1:4[44] (Figure 3). These results strongly favour the $Be_4O(OOCCH_3)_6$-like structure with one of the acetato groups replaced by the alkoxo ligand. Notwithstanding the fact that the compound contains an undoubtedly strained 4-membered cycle



it is quite stable, can be stored in the air, melts and even sublimes under normal pressure conditions without decomposition. One may wonder if the stability of this compound can be attributed to improved planarity of the 6-membered cycles

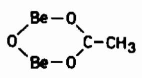
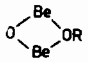


Figure 3. Proton NMR spectra of $Be_4O(OOCCH_3)_6$ (1), $Be_4O(OOCCH_3)_5OC_2H_5$ (2), $Be_7O_2(OOCCH_3)_8(OH)_2$ (3), $Be_6O_2(OOCCH_3)_8$ (4), and $Be_5O_2(OOCCH_3)_6$ (5).

as compared to basic beryllium acetate. We have mentioned above that these are nonplanar in the $Be_4O(OOCCH_3)_6$ molecule, with a dihedral angle between the BeOBe and OCO planes of *ca.* 10.5°. The removal of one of the acetato groups makes possible the formation of the planar cycles at the expense of a decrease of the vacant BeOBe angle to about 100°, provided the bond distances and OCO and OBeO angles remain the same as in the basic acetate molecule (Table I). In view of these considerations, the substitution of one of the acetato groups of the $Be_4O(OOCCH_3)_6$ molecule with an alkoxy one may seem not very unfavourable after all, despite a distortion of the OBe_4 tetrahedron.

It is interesting that the fragments of the composition $Be_4O(OOCCH_3)_5^+$ give the most intense ion currents and are the heaviest units in the mass spectrum of $Be_4O(OOCCH_3)_6$ whereas no molecular ions appear (Vogel and Hobrock[45]).

Detailed analysis of the vibrational spectrum of oxomonoalkoxoderivatives[11] represents a rather involved problem. The spectrum is much simpler than that predicted from symmetry considerations, probably owing to accidental degeneracies. Nevertheless, it proved possible to identify the bands in the region of beryllium–oxygen vibrations which are sensitive to changes of the radical R in $Be_4O(OOCCH_3)_5OR$ and which therefore may be thought to correspond to vibrations of the 4-membered cycle



B. *μ_4-Oxomono-μ-hydroxopenta-μ-acetatotetraberyllium*

Like alkoxoacetates, beryllium hydroxoacetate undergoes thermolysis to yield volatile $Be_4O(OOCCH_3)_5OH$, albeit in a very low yield. Hydrolysis of beryllium dioxohexaacetate (see Section 4.C) in chloroform solution provides a more convenient synthetic route to this product[46]. The purification procedure involves vacuum sublimation at 170° C (5×10^{-2} mm Hg) and recrystallization of the sublimate from benzene.

The compound has been assigned the structure of its alkoxo analog on the basis of close similarity in composition, properties and vibrational spectra of the two compounds[46]. The higher sublimation temperature of $Be_4O(OOCCH_3)_5OH$ may be attributed to the effect of hydrogen bonding. In fact, chloroform solutions of this compound give a 150 cm^{-1} higher frequency shift of the OH stretches from the value observed for crystalline samples, probably because of cleavage of hydrogen bonds.

4. Beryllium Di-μ_4-oxoacetates

A. *Di-μ_4-oxodi-μ-hydroxoocta-μ-acetatoheptaberyllium*

Decomposition of the pyridine adduct of beryllium hydroxoacetate at 160–170° C under dry air at normal pressure yields a mixture of products which, after the removal of beryllium oxomonohydroxopentaacetate by sublimation and recrystallization of the residual product from hot water-free benzene, yields colourless needle-like crystals of $Be_7O_2(OOCCH_3)_8(OH)_2$[47]. The molecular weight determinations yield values corresponding to one formula unit. The IR spectra of the compound show it to contain the BeO_4 tetrahedra, bridging acetato ligands, and OH groups participating in hydrogen bonding (dissolving the product in chloroform results in a 150 cm^{-1} higher frequency shift of the OH stretching vibrations). The NMR spectrum (Figure 3) reveals the occurrence of three types of acetato ligands in the ratio of 1:2:1. The molecular model that fits these experimental results is shown in Figure 4. The model has been derived on the assumption that the most important geometrical parameters of the basic acetate molecule (see Table I) should retain their values over the series of beryllium μ_4-oxoacetato complexes. We followed this principle in considering possible structures of $\mu_4$oxo derivatives in all cases. The basic feature of the structure shown in Figure 4 is the presence of two OBe_4 tetrahedra sharing an apex. In agreement with the NMR results, the three sets of the acetato groups differing in their environment include 2, 4, and 2 ligands, respectively.*

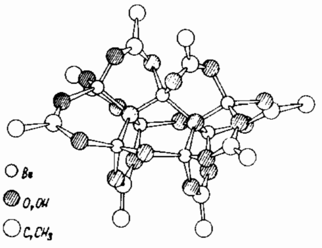


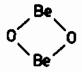
Figure 4. Molecular structure of $Be_7O_2(OOCCH_3)_8(OH)_2$.

$Be_7O_2(OOCCH_3)_8(OH)_2$ dissolves in hot pyridine to yield, after careful removal of excess solvent, precipitates of the composition $Be_7O_2(OOCCH_3)_8(OH)_2 \cdot 2py$ which appear to contain pyridine molecules hydrogen bonded to the OH ligands, similarly to the case of the pyridine derivative of beryllium hydroxoacetate.

B. *Di-μ_4-oxoocta-μ-acetatohexaberyllium*

Thermal decomposition of the amine complexes $Be_3O(OOCCH_3)_4 \cdot 3RNH_2$ (see Section 2.C.) at 100° *in vacuo* (5×10^{-2} mm Hg) leads to the removal of all the amine molecules. The residual product purified by Soxhlet extraction with n-pentane is soluble in organic solvents better than basic beryllium acetate (chloroform, benzene, carbon tetrachloride), not hygroscopic, sublimes under vacuum at about 120 to 140° C, and melts (with decomposition) at 215° C[48]. The product crystallizes from refluxing n-pentane solutions in the form of colourless needles (β-form) which gradually transform to prysmatic crystalls of the α crystal modification under mother liquor. According to the high-temperature X-ray data[49], the $\alpha \rightarrow \beta$ phase transition occurs at 148° C. The β form can exist at ambient temperature indefinitely long in the absence of solvents. The α form crystallizes in the triclinic lattice ($a = 10.0, b = 10.0, c = 13.5$ Å; $\alpha = 72, \beta = 90, \gamma = 76°$; $Z = 2$) while crystals of the β modification belong to the hexagonal system ($a = 41.8, c = 10.2$ Å; $Z = 24$). The Z values correspond to dimeric units $Be_6O_2(OOCCH_3)_8$. The dimeric structure has been determined on the basis of molecular weight measurements in benzene solutions.

A structure containing bridging acetato groups and tetrahedral beryllium atoms can be predicted for this compound from its vibrational spectrum[11]. The observed spectrum closely resembles that of basic beryllium acetate and, in addition, exhibits some features characteristic of the 4-membered cycle



In Figure 5, the molecular model with the D_2 symmetry is shown which is consistent with spectral data and satisfies steric requirements. Other models either fail to explain the observed spectrum or suggest unreasonable values for some of the molecular parameters.

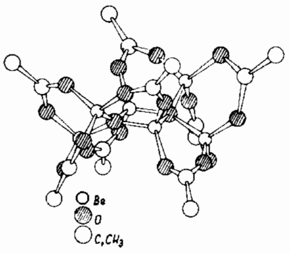


Figure 5. Molecular structure of $Be_6O_2(OOCCH_3)_8$.

The model predicts the occurrence of two types of acetato groups in the molecule in the ratio of 1 : 1 and thus fully agrees with the NMR results (Figure 3).

Solvolysis of dioxooctaacetate with water and alcohols in chloroform solutions yields a mixture of basic beryllium acetate and its monosubstituted derivatives (hydroxo- and alkoxo-, respectively). Pure water-free ethanol reacts with dioxooctaacetate to yield beryllium ethoxoacetate.

The interaction of beryllium dioxooctaacetate with primary amines[50] (but not with ammonia) is the only known example of the fully reversible solvolysis of beryllium acetato derivatives. Thermal decomposition of the products leads to the recovery of the initial compound. The composition of the complexes corresponds to the formula $Be_6O_2(OOCCH_3)_8 \cdot 4RNH_2$ and their structure can be written as shown in Figure 6[50]. The structure explains satisfactorily the difference in thermal stability between the ammonia and amine complexes of beryllium dioxooctaacetate which lends

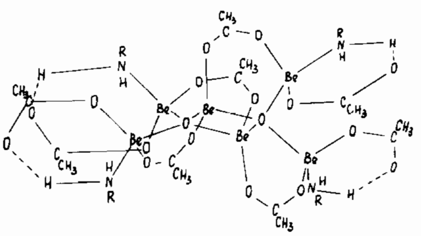


Figure 6. A possible structure model for $Be_6O_2(OOCCH_3)_8 \cdot 4RNH_2$.

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*The four approximately equivalent acetato ligands included in one of these groups occupy two different sets of equivalent positions in the molecule which explains a distinct splitting of the corresponding NMR peak into two components (Figure 3).

support to the proposed model. The ammonia derivative contains 6 NH_3 molecules and hence by two acetato bridges binding the OBe_4 tetrahedra less than complexes with primary amines[51], which predicts a lower stability of the inorganic skeleton in the ammino derivative. Actually, when heated, this complex undergoes a deeper decomposition than its amine analogs.

The vibrational spectra of the amine complexes retain the principal features characteristic of the parent molecule but indicate the presence of both bridging and monodentate acetato groups. The corresponding Raman lines are of approximately equal intensity which, though not providing a decisive structural evidence, seems to agree better with the structure shown in Figure 6 than with other models otherwise possible (the latter suggest the presence of bi- and monodentate acetato group in a 3 : 1 ratio).

The IR spectra of the complexes in the region of the CO stretches are indicative of strong hydrogen bonding between the amine molecule and the carboxyl group, similarly to the case of the corresponding complexes of beryllium acetate (see Section 2.C). Six-membered cycles incorporating such bonds seem to be very stable. It is likely that the tendency for the formation of cycles of this type plays an important role in determining both the direction of reactions of beryllium acetato complexes with ammonia and fatty amines and the composition of the reaction products.

C. Di-μ_4-oxohexa-μ-acetatopentaberyllium

Thermolysis of beryllium dioxooctaacetate at temperatures above its melting point (215° C) leads to the formation of a mixture containing basic beryllium acetate as one of the components. The latter quantitatively sublimes under vacuum at temperatures below 200° C. The remaining substance is an air-stable compound of the composition $Be_5O_2(OOCCH_3)_6$[52], soluble in chloroform and ethane dichloride and sublimable at temperatures higher than 240° C. The compound melts under pressure at 300° C with decomposition to a mixture containing, in particular, BeO and $Be_4O(OOCCH_3)_6$. The molecular weight measurements show that chloroform solutions of beryllium dioxohexaacetate contain monomeric units.

Since approximately equimolecular quantities of basic beryllium acetate and beryllium dioxohexaacetate are formed in the thermal decomposition of beryllium dioxooctaacetate, the following equation can be written:

$$3Be_6O_2(OOCCH_3)_8 \xrightarrow{t \geqq 215^\circ C} 2Be_5O_2(OOCCH_3)_6 + 2Be_4O(OOCCH_3)_6$$

Arguments similar to those applied in the case of other μ_4-oxoderivatives seem to favour the structure shown in Figure 7 for this compound[52]. The NMR spectrum (Figure 3) fits the proposed model: the occurrence of only one proton NMR signal in this case (like in the case of basic beryllium acetate) indicates all the acetato groups involved to be equivalent. Thus one more (and the last possible) mode of condensing the OBe_4 tetrahedra is realized in $Be_5O_2(OOCCH_3)_6$: as we have seen, the adjacent OBe_4 groups can share an apex (dioxodihydroxooctaacetate), an edge (dioxooctaacetate) and a face (dioxohexaacetate). Steric strain in the frame (and hence the reactivity of di-μ_4-oxo derivatives, see the next Section) should grow rapidly across this series. Three of a total of 6 valence angles at the "tetrahedral" oxygen atoms cannot be greater than 80° in the face condensed structure. Still, the reactivity of the compound is of a somewhat "latent" character thanks to the screening effect of the outer organic groups. Thus, when treated with water, alcohols, or amines at room temperature $Be_5O_2(OOCCH_3)_6$ remains intact for a considerable time because of its low solubility in polar media. However, beryllium dioxohexaacetate readily and quantitatively reacts with trace amounts of water and alcohols in chloroform solutions.

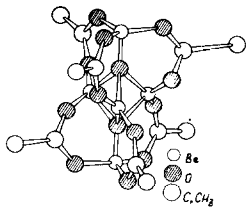


Figure 7. Molecular structure of $Be_5O_2(OOCCH_3)_6$.

5. Solvolysis of μ_4-Oxoacetates

Solvolysis of beryllium μ_4-oxoacetates with water and ethanol has been studied in chloroform solutions at 23 ± 1° C spectrophotometrically utilizing characteristic IR absorption bands at about 500 cm^{-1}[53]. The results obtained from intensity measurements are shown in Figure 8.

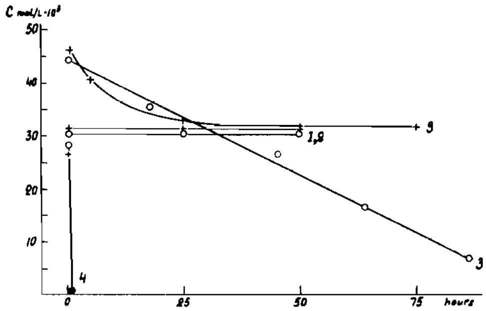


Figure 8. Kinetics of solvolysis of $Be_4O(OOCCH_3)_6$ (1), $Be_7O_2(OOCCH_3)_8(OH)_2$ (2), $Be_6O_2(OOCCH_3)_8$ (3), and $Be_5O_2(OOCCH_3)_6$ (4) with water (circlets) and ethanol (crosses).

Basic beryllium acetate and beryllium dioxodihydroxooctaacetate appear to be practically nonreactive towards both water and alcohol. The IR spectra of these compounds do not change with time in water–chloroform and ethanol–chloroform solutions over the whole spectral interval studied (400 to 4000 cm^{-1}). $Be_6O_2(OOCCH_3)_8$ reacts with ethanol rather slowly and the equilibrium point corresponds to approximately 30% conversion. Water decomposes this compound quantitatively during a period of several days. The hydrolysis seems to proceed via the rate determining step of monomolecular decomposition.

In the case of dioxohexaacetate, a rapid decomposition occurs under the action of both water and alcohol with the formation of monosubstituted μ_4-oxo derivatives.

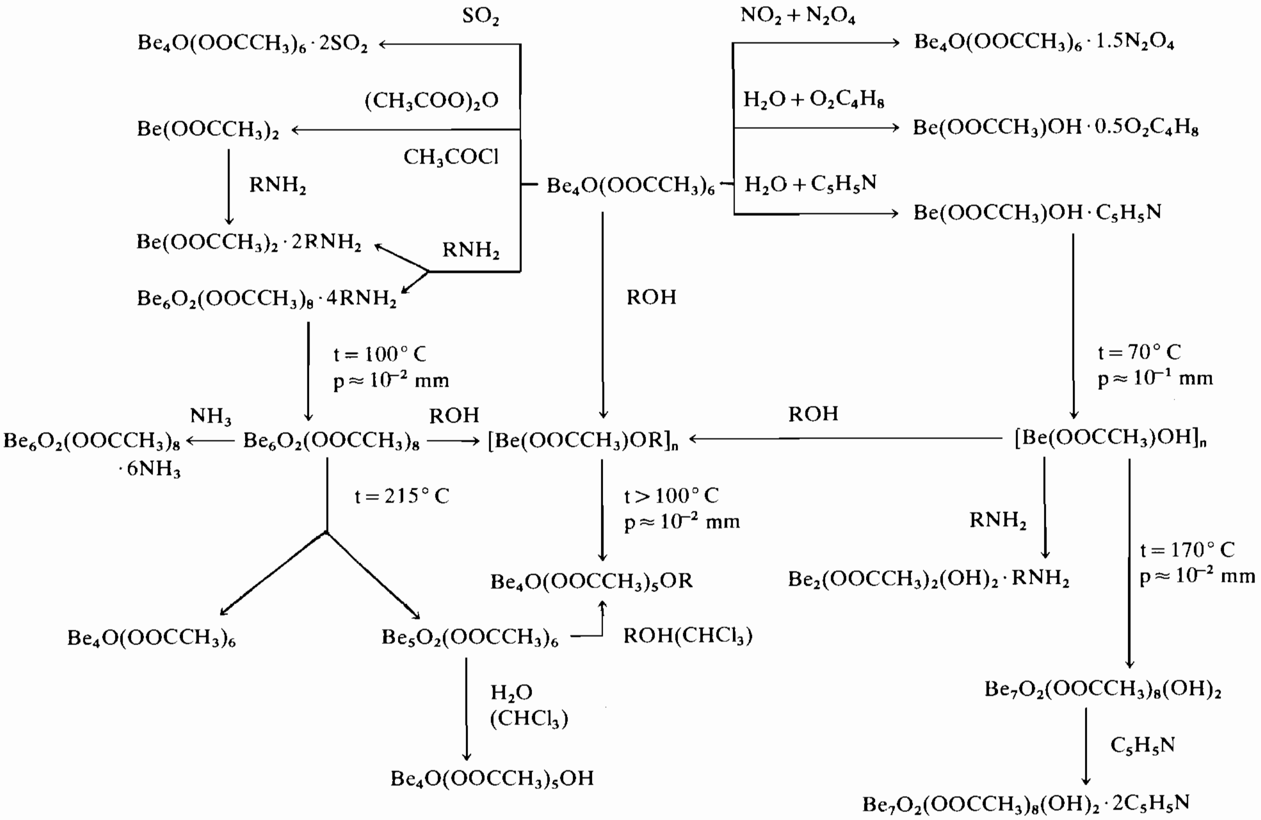
Thus, the rate of the solvolysis increases across the series: $Be_4O(OOCCH_3)_6 \approx Be_7O_2(OOCCH_3)_8(OH)_2 < Be_6O_2(OOCCH_3)_8 < Be_5O_2(OOCCH_3)_6$, which can be rationalized in terms of increasing steric strain or increasing accessibility of the Be atoms to attacks by nucleophiles.

6. Conclusion

The following Scheme summarizes our present knowledge of the chemical potential of basic beryllium acetate and its structure analogs. There is no doubt that other structure combinations of the OBe_4 tetrahedra with such bridging ligands as RCOO, RO, and OH are possible and that the range of beryllium μ_4-oxo compounds will be extended. In particular, this is true of alkoxoacetato derivatives. Recently isolated $Be_7O_2(OOCCH_3)_6(OC_2H_5)_4$ provides an example[54].

Properties of beryllium acetato derivatives vary within rather wide limits, and their variation over the series of compounds studied merits interest. A number of factors appear to be responsible for the observed patterns. These include changes in ionic nature of the Be–O bonds, in bond configuration at the Be and μ_4-O atoms, in the accessibility of the Be atoms to nucleophilic attacks, and in the nature of outer ligands screening the Be–O skeleton. Of course, it is hardly possible to discriminate between these factors since, say, the nature of Be–O bonding must depend on both

Reactions of Beryllium μ_4-oxo Derivatives



the nature of the ligands involved (their electron-donor potential) and the geometry of a given coordination polyhedron (the type of hybridization of AO's involved).

According to the X-ray electron spectroscopy data[55], covalency of the Be–O bonds increases, depending on the ligand, in the series: $CH_3COO < OH < O < OC_2H_5$. On the other hand, according to the same data, the effective charge on the Be atom undergoes no significant change in going from $Be_4O(OOCCH_3)_6$ to $Be_7O_2(OOCCH_3)_8(OH)_2$, $Be_6O_2(OOCCH_3)_8$, or $Be_5O_2(OOCCH_3)_6$. Hence the observed reactivity pattern (Section 5) must be explained by changes in steric characteristics of the Be–O skeleton.

Other factors seem to control solubility and volatility patterns. Basic beryllium acetate has a somewhat higher solubility in non-polar media than $Be_5O_2(OOCCH_3)_6$ but is considerably less soluble than $Be_6O_2(OOCCH_3)_8$. The same is true of the volatility of these compounds. Substitution of acetato groups with alkoxo ligands results in a rapid increase of both solubility and volatility of beryllium μ_4-oxo derivatives. According to their solubility in n-pentane, the compounds studied may be ordered as follows: $Be_5O_2(OOCCH_3)_6 \approx Be_4O(OOCCH_3)_6$ (practically insoluble) $< Be_6O_2(OOCCH_3)_8 < Be_4O(OOCCH_3)_5OC_2H_5$ (markedly soluble) $\ll Be_7O_2(OOCCH_3)_6(OC_2H_5)_4$ (solubility of about 30%). Thus, the ligand nature appears to be a predominant factor in determining solubility and volatility of low weight molecular beryllium oxoacetates.

On the contrary, thermal stability of the compounds in question seems to depend primarily on the stability of the inorganic frame. The occurrence of two adjacent OBe_4 units containing rather polar Be–O bonds in the molecule of di-μ_4-oxo derivatives appears to be unfavourable thermodynamically, and the corresponding structures easily collapse to yield mono-μ_4-oxo fragments.

In general, the chemistry of beryllium acetato derivatives is governed by the preference of the divalent Be atom for the formation of coordination tetrahedra and hence for utilizing the donor potential of the ligands. Six-membered cycles exceedingly characteristic of beryllium stereochemistry provide the most favourable conditions for charge redistribution and the formation of coordination tetrahedra. It may well be that thermodynamic stability of these cycles is responsible for the stability of such unusual molecular compounds as basic beryllium acetate and its structure analogs containing four-coordinate oxygen atoms.

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