Syntheses and Properties of Zinc and Calcium Complexes of Valinate and Isovalinate: Metal α-Amino Acidates as Possible Constituents of the Early Earth's Chemical Inventory

Henry Strasdeit,* Insa Büsching, Sabine Behrends, Wolfgang Saak, and Walter Barklage[a]

Abstract: We have studied the ligand behavior of racemic isovalinate (iva$^-$) and valinate (val$^-$) towards zinc(II) and calcium(II). The following solid metal amino acidates were obtained from aqueous solutions: $Zn_3Cl_2(iva)_4$ (**1**), $Zn_3Cl_2(val)_4$ (**2**), $Zn(val)_2$ (**3**), $Zn(iva)_2 \cdot 2H_2O$ (**4**), $Zn(iva)_2 \cdot 3.25H_2O$ (**5**), $Zn(iva)_2$ (**6**), $Ca(iva)_2 \cdot xH_2O$ (**7**), and $Ca(val)_2 \cdot H_2O$ (**8**). Except for complex **3**, these were hitherto unknown compounds. The conditions under which they formed, together with current ideas of the conditions on early Earth, support the assumption that α-amino acidate complexes of zinc and calcium might have belonged to early Earth's prebiotic chemical inventory. The zinc isovalinates **1**, **4**, and **5** were characterized by X-ray crystal structure analyses. Complex **1** forms a layer structure containing four- and five-coordinate metal atoms, whereas the zinc atoms in **4** and **5** are five-coordinate. Compound **5** possesses an unprecedented nonpolymeric structure built from cyclic $[Zn_6(iva)_{12}]$ complexes, which are separated by water molecules. The thermolyses of solids **1**, **3**, and **8** at 320 °C in an N_2 atmosphere yielded numerous organic products, including the cyclic dipeptide of valine from **3** and **8**. Condensation, C–C bond breaking and bond formation, aromatization, decarboxylation, and deamination reactions occurred during the thermolyses. Such reactions of metal-bound α-amino acidates that are abiotically formed could already have contributed to an organic-geochemical diversity before life appeared on Earth.

Keywords: amino acids · coordination modes · prebiotic chemistry · thermolysis · zinc

Introduction

The current paradigm for the origin of life states that on early Earth abiotically formed organic compounds were present that constituted the raw material from which the first metabolizing and self-replicating systems evolved.[1, 2] α-Amino acids are among the most intriguing of the supposed prebiotic molecules. As Miller and Urey demonstrated in their classical experiments, amino acids are formed by electric discharges in an atmosphere of a mixture of CH_4, NH_3, H_2, and H_2O.[3] From a more recent view, however, the atmosphere at the time before life's origin was dominated by N_2, CO_2, and H_2O with lesser amounts of CO, H_2, and possibly CH_4. In such a weakly reducing atmosphere, amino acid formation appears to be more difficult.[4]

Alternatively, comets and meteorites could have been major sources of amino acids (and other organics), either by delivery or by impact-shock synthesis.[5] The possibility of a direct supply gains support from the detection of amino acids in certain carbon-rich meteorites, the carbonaceous chondrites.[6] The Murchison meteorite, for example, contains at least 66 different amino acids.[7] Some of the amino acids there as well as in the Murray meteorite have been reported to exhibit small excesses of the L-enantiomers.[8, 9] However, terrestrial contaminations could largely be excluded. This has been shown, inter alia, by analyses of the stable isotopes of nitrogen and carbon in the individual enantiomers.[10, 11] Thus, both the D- and L-forms are of extraterrestrial origin. Carbonaceous chondrites are considered to be composed of primitive material from the early times of the solar system. Furthermore, the isotopic compositions suggest that the amino acids or their precursors were abiotically formed in the interstellar cloud that preceded the solar system.[12]

These considerations, taken together, give rise to the assumption that amino acids belonged to Earth's early chemical inventory and therefore were among the first organic compounds capable of forming stable metal complexes.[13] In the present paper, we describe the syntheses, structures, and thermal behavior of zinc and calcium complexes of racemic isovalinate and valinate. Zinc(II) and calcium(II), which both have numerous biological functions in modern organisms,[14] were chosen because of their possible

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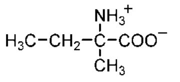
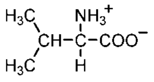
[a] Prof. Dr. H. Strasdeit, Dr. I. Büsching, Dipl.-Chem. S. Behrends,
Dipl.-Chem. W. Saak, Dr. W. Barklage
Fachbereich Chemie der Universität
Carl-von-Ossietzky-Str. 9–11, 26129 Oldenburg (Germany)
Fax: (+49) 441-798-3329
E-mail: henry.strasdeit@uni-oldenburg.de

availability in the ocean and/or at the surface of the early Earth (see the discussion below). Isovaline (Hiva) and valine (Hval) belong to the ten most abundant amino acids in the Murchison meteorite.[7]



Hiva



Hval

Unlike valine, isovaline is a nonprotein amino acid that is exceedingly rare in the biosphere.[15] It therefore closely approaches the concept of an "extraterrestrial" substance.

Results and Discussion

Syntheses of the metal complexes: In aqueous solution, calcium(II) and zinc(II) α-amino acidato complexes are only moderately stable if additional donors in the amino acid sidechains are absent.[16] It is therefore necessary to raise the natural acidic pH value of the M^{II}/amino acid systems. One possible way to achieve this is the use of the urea hydrolysis technique, which has previously been used to prepare Cu^{II} amino acidates.[17] This method has the advantage that, by slow release of ammonia, crystallization of the products proceeds in a controlled manner. When a 1:2:1 molar ratio of zinc(II) chloride, *rac*-isovaline (Hiva), and urea was kept at 80 °C in aqueous solution, the unexpected mixed chloride/isovalinate $Zn_3Cl_2(iva)_4$ (**1**) crystallized in good yield [Eq. (1)].

Abstract in German: *Wir haben untersucht, wie sich racemisches Isovalinat (iva⁻) und Valinat (val⁻) als Liganden gegenüber Zink(II) und Calcium(II) verhalten. Aus wässriger Lösung wurden die folgenden festen Metall-Aminoacidate erhalten:* $Zn_3Cl_2(iva)_4$ *(**1**),* $Zn_3Cl_2(val)_4$ *(**2**),* $Zn(val)_2$ *(**3**),* $Zn(iva)_2 \cdot 2H_2O$ *(**4**),* $Zn(iva)_2 \cdot 3.25H_2O$ *(**5**),* $Zn(iva)_2$ *(**6**),* $Ca(iva)_2 \cdot xH_2O$ *(**7**) und* $Ca(val)_2 \cdot H_2O$ *(**8**). Mit Ausnahme von **3** handelt es sich hierbei um bisher unbekannte Verbindungen. Die Bedingungen, unter denen sie entstanden, stützen—in Kombination mit gegenwärtigen Vorstellungen über die Erdgeschichte—die Annahme, dass Zink- und Calcium-α-Aminoacidate möglicherweise zum präbiotischen chemischen Inventar der Urerde gehörten. Die Zink-Isovalinate **1**, **4** und **5** wurden durch Röntgenkristallstrukturanalysen charakterisiert. Komplex **1** bildet eine Schichtenstruktur, die vier- und fünffach koordinierte Metallatome enthält. Die Zinkatome in **4** und **5** sind fünffach koordiniert. Verbindung **5** besitzt eine nichtpolymere Struktur, die bislang ohne Beispiel ist. Sie ist aus cyclischen* $[Zn_6(iva)_{12}]$*-Komplexen aufgebaut, die durch Wassermoleküle separiert sind. Die Thermolysen von festem **1**, **3** und **8** bei 320 °C in einer* N_2*-Atmosphäre ergaben zahlreiche organische Produkte, zum Beispiel aus **3** und **8** das cyclische Dipeptid des Valins. Während der Thermolysen traten Kondensationsreaktionen, C–C-Bindungsbruch und -Bindungsbildung, Aromatisierung, Decarboxylierung und Deaminierung auf. Solche Reaktionen metallgebundener, abiotisch entstandener α-Aminoacidate könnten zu einer organisch-geochemischen Vielfalt beigetragen haben, noch bevor Leben auf der Erde existierte.*

$$3\,ZnCl_2 + 4\,Hiva + 2\,(NH_2)_2CO + 2\,H_2O \xrightarrow{80\,^{\circ}C} Zn_3Cl_2(iva)_4\ (\mathbf{1})\downarrow + 4\,NH_4Cl + 2\,CO_2\uparrow \qquad (1)$$

The corresponding reaction system with *rac*-valine (Hval) behaves differently: initially, compound $Zn_3Cl_2(val)_4$ (**2**), which is analogous to **1**, crystallizes. Later on, when the solution is depleted in zinc chloride relative to Hval, the already known compound $Zn(val)_2$ (**3**) precipitates.[18] It is, however, possible to obtain pure **2** and **3** in moderate and very good yields, respectively, by the addition of excess chloride (as sodium chloride) and of Hval, respectively. Another route to **3** uses zinc nitrate instead of the chloride.

As an alternative to the urea hydrolysis technique, a suspension of the metal oxide or hydroxide may be heated under reflux together with the amino acid. This method allows the preparation of $Zn(iva)_2 \cdot 2H_2O$ (**4**) and $Zn(iva)_2 \cdot 3.25H_2O$ (**5**) from zinc oxide [Eq. (2)] ($n = 2$ for **4**, $n = 3.25$ for **5**).

$$ZnO\ (excess) + 2\,Hiva \xrightarrow[reflux]{H_2O} Zn(iva)_2 \cdot n\,H_2O \qquad (2)$$

Both **4** and **5** can only be isolated in low yields. When the volume of the reaction solution is reduced too far, the products are contaminated by unreacted amino acid. Once isolated, **5** very rapidly looses water of crystallization. The water content given in the formula was therefore deduced from the crystal structure analysis (see below). In order to obtain a well-defined product it is advisable to convert **5** into the anhydrous form $Zn(iva)_2$ (**6**) in a vacuum. Another problem with compound **5** is its apparently kinetically controlled formation. For this reason, the preparative method sometimes fails and gives **4** instead of **5**. Fortunately, the two compounds are easily distinguishable by their different crystal forms (see Experimental Section). Compound **4** can also be prepared from zinc hydroxide. In the same way, but with better yields, $Ca(iva)_2 \cdot xH_2O$ (**7**) and $Ca(val)_2 \cdot H_2O$ (**8**) are accessible from calcium hydroxide and the respective amino acid. Analytical data for **7** best fit the hemihydrate, though the water content of freshly isolated crystals is probably higher.

Transferability to prebiotic environmental conditions: Factors crucial to the existence of zinc and calcium amino acidates on the early Earth are i) the acidity and temperature of the hydrosphere, ii) the chemical availability of the metal ions, and iii) the presence of amino acids. The latter aspect has already been discussed in the Introduction. Values of pH 5.5–8 and 55–80 °C have been assumed for the ocean existing $\approx 4 \times 10^9$ years ago.[19, 20] Conditions under which the zinc chloride amino acidates **1** and **2** can be prepared fall within these ranges: namely, **1** and **2** crystallize at 80 °C and at pH 6 and 5.5, respectively. They are sparingly soluble in water. Thus their precipitation can be regarded as an efficient way of accumulating isovaline and valine from dilute solutions. The amino acids themselves are readily soluble in water.

In contrast to **1** and **2**, the calcium compounds **7** and **8** are readily soluble in water. Their solutions have pH values of 9–

10, which may be compared to pH 8 of similarly concentrated solutions of the zinc isovalinates **4**–**6**. The more ionic character of dissolved **7** and **8** is not only reflected by the basicity of their solutions, but also by the ^{13}C NMR chemical shifts which are within ± 0.2 ppm of the values of the respective NMe_4^+ amino acidate. In contrast, the ^{13}C NMR peak positions of the zinc compound **6** differ by up to 3.5 ppm from those of $NMe_4^+(iva)^-$. This data indicates a comparatively weak complex formation with calcium(II). In order to obtain more quantitative information, we used the program SPE[21] to calculate the species distribution in the calcium(II)/alanine(Hala) system for a total concentration of 0.10 M of each of the two components at 25 °C. Alanine was chosen because it appears to be the only non-*N*-substituted α-alkyl α-amino acid for which at least the stability constant of the 1:1 complex with calcium is known.[16] Our calculations show that this complex, namely $[Ca(ala)]^+$, is practically absent at pH 7.0. At pH 8.0 it contains 3% of the total calcium. This percentage increases to 18% at pH 9.0. Evidently, the formation of **7** and **8** on early Earth is conceivable when the (local) existence of concentrated solutions of relatively high pH is assumed.

The chemical availability of calcium(II) in the Archaen ocean was possibly affected by the presence of carbon dioxide. High atmospheric partial pressures of CO_2 have been proposed because CO_2, being a greenhouse gas, could have prevented global glaciation of the early Earth at a time when the solar luminosity was lower than today.[4b,c] But there are also other solutions to the "faint young Sun–frozen Earth" paradox that do not depend on the assumption of high atmospheric CO_2 levels.[20b, 22] The sedimentary rock record is consistent with marine calcium(II) concentrations of 0.01–0.3 M at pH 7.0 and at $\approx$3–100 times the present atmospheric level (PAL) of CO_2.[23] Even at higher pH values, such relatively high concentrations of dissolved calcium(II) were still possible, but they required a lower upper limit of the CO_2 partial pressure. So both the calcium(II) concentration and the pH could have been sufficient for calcium amino acidate formation. Our attempts to obtain calcium α-amino acidates from calcite ($CaCO_3$) and simple α-amino acids were unsuccessful. It can be concluded that the huge amounts of solid calcium carbonate, which must already have existed on early Earth, were not directly available for amino acidate formation, at least when those amino acids are concerned that lack additional functional groups.

The availability of zinc might have been limited by the formation of $ZnCO_3$ and ZnS, which both are poorly soluble. At pH 7.0 and $\approx$3–100 times PAL of CO_2 (see above), the resulting dissolved carbonate would have allowed a zinc(II) concentration of ≤ 0.04 mM.[24] This is 3–4 orders of magnitude lower than the calcium(II) concentration. However, as far as the comparative values are known,[16] stability constants of zinc amino acidates are higher than those of calcium amino acidates typically by about this factor. Because of the mildly reducing atmosphere on early Earth, sulfur was mainly present in the oxidation state −II, initially as H_2S from volcanic sources. Metal sulfide formation was an important sink for H_2S. In particular, the formation of the extremely stable and highly insoluble pyrites (FeS_2) from FeS and H_2S[25] could have efficiently lowered local H_2S concentrations. This might have allowed zinc(II) concentrations to be high enough for zinc amino acidate formation, despite the rather small solubility product of ZnS.

Characterization: The complexes described here are most conveniently identified by infrared spectroscopy. Prominent features in the IR spectra are two very strong bands, one slightly below and the other slightly above $\tilde{\nu} = 1600\,cm^{-1}$. These absorptions are attributed to $\delta(NH_2)$ and $\nu(C{=}O)$ [or $\nu_{as}(COO^-)$] modes.[26] Comprehensive IR spectroscopic studies of some *rac*-valinato and *rac*-isovalinato complexes, including **3**, have been performed by others.[18, 27] The IR spectra of the zinc isovalinates **4** and **6** closely resemble each other. Because of rapid efflorescence, no reliable IR spectrum can be recorded for the third zinc isovalinate **5**. As mentioned above, **4** and **5** can, however, be distinguished by their different crystal shapes.

In order to find out how the unusual composition of $Zn_3Cl_2(iva)_4$ (**1**) and the different contents of water of crystallization in $Zn(iva)_2 \cdot 2H_2O$ (**4**) and $Zn(iva)_2 \cdot 3.25H_2O$ (**5**) are reflected in the solid-state structures, single-crystal X-ray structure analyses were performed on these compounds. To the best of our knowledge, crystal structures of isovalinato complexes have not been previously determined. Apparently, the solid-state structure of isovaline itself is also unknown,[28] while the crystal structures of some organic derivatives have been determined, for example, *N*-acetyl-(*S*)-isovaline[29] and some isovaline homopeptides.[30] We were unable to grow suitable single crystals of the calcium isovalinate **7**; however, we were able to determine the structure of the valinato complex $Ca(val)_2 \cdot H_2O$ (**8**). Complex **8** forms a one-dimensional coordination polymer built from carboxylate-bridged seven-coordinate calcium(II) ions. Details of this structure will be reported elsewhere, together with the crystal structures of other calcium α-amino acidates.[31]

Crystals of **1** consist of layers perpendicular to the crystallographic *c* direction (Figure 1). Neighboring layers are connected only by van der Waals contacts in alkyl sidechains. Two types of zinc ions can be discerned: one is found in $\{ZnCl(iva)_2\}^-$ groups (Zn1), while the other (Zn2) links these groups in two dimensions. The overall coordination architecture may therefore be expressed by the formula $^2_\infty[Zn\{ZnCl(iva)_2\}_2]$. The valinate $Zn_3Cl_2(val)_4$ (**2**) and **1** are probably isostructural, as judged from the powder diffraction patterns.

In **1**, Zn1 is situated in a ClO_2N_2 environment (Figure 2). On the basis of the angular criterion τ, as defined by Addison et al. ($\tau = 1.00$ for an ideal trigonal bipyramid and $\tau = 0.00$ for an ideal square pyramid),[32] the coordination polyhedron around Zn1 is a strongly distorted trigonal bipyramid ($\tau = 0.67$). Compounds that possess $ZnClO_2N_2$ groups are rare. The Cambridge Structural Database (CSD)[28] lists only four examples, of which the mononuclear complex [ZnCl(pic)(Hpic)] (Hpic = picolinic acid)[33] shows the strongest resemblance to the $\{ZnCl(iva)_2\}^-$ moiety of **1**. The second type of zinc ion in **1**, Zn2, is situated at the center of a strongly tetragonally compressed O_4 tetrahedron. The corresponding bond length of 2.004(2) Å (Zn2–O1) is larger than the mean value of 1.946(22) Å observed in ZnO_4 groups in which the O atoms

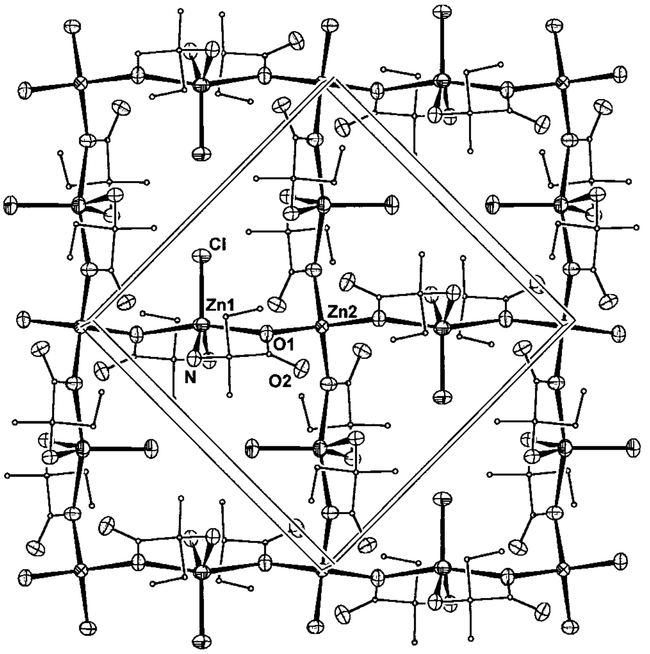


Figure 1. Layer of $Zn_3Cl_2(iva)_4$ (**1**) viewed approximately down the *c* axis. The unit cell is shown. Hydrogen atoms are omitted.

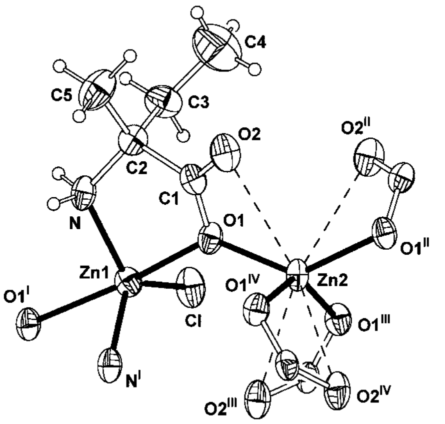


Figure 2. The coordination environments of the zinc atoms in $Zn_3Cl_2(iva)_4$ (**1**). Displacement ellipsoids are shown at the 50% probability level. Bond lengths [Å] and angles [°]: Zn1−Cl 2.223(1), Zn1−O1 2.242(2), Zn1−N 2.028(3), Zn2−O1 2.004(2), Zn2 ··· O2 2.794(2); Cl-Zn1-O1 98.01(6), Cl-Zn1-N 123.76(9), O1-Zn1-$O1^{I}$ 164.0(1), O1-Zn1-N 77.7(1), O1-Zn1-N^{I} 93.4(1), N-Zn1-N^{I} 112.5(2), O1-Zn2-$O1^{II}$ 135.9(2), O1-Zn2-$O1^{III}$ 98.10(6). Symmetry transformations: (I): $0.5-y, 0.5-x, -z$; (II): $1-x, 1-y, z$; (III): $y, 1-x, -z$; (IV): $1-y; x, -z$.

belong to terminal monodentate alkylcarboxylates.[34] Factors which can lead to this small, but significant bond elongation are the bridging function of O1, increased O ··· O repulsion caused by the flattening of the coordination tetrahedron, and, in particular, a weak coordination of the O2 atoms. The distance Zn2 ··· O2 (2.794(2) Å) is smaller than the sum of the van der Waals radii (2.9–3.0 Å)[35] and is thus indicative of weak "secondary" bonding. The carboxylate groups can therefore be described as being aniso-bidentate near the monodentate extreme. As Harding recently pointed out, zinc carboxylates show the full range of intermediates between symmetrical bidentate and *syn*-monodentate coordination.[36]

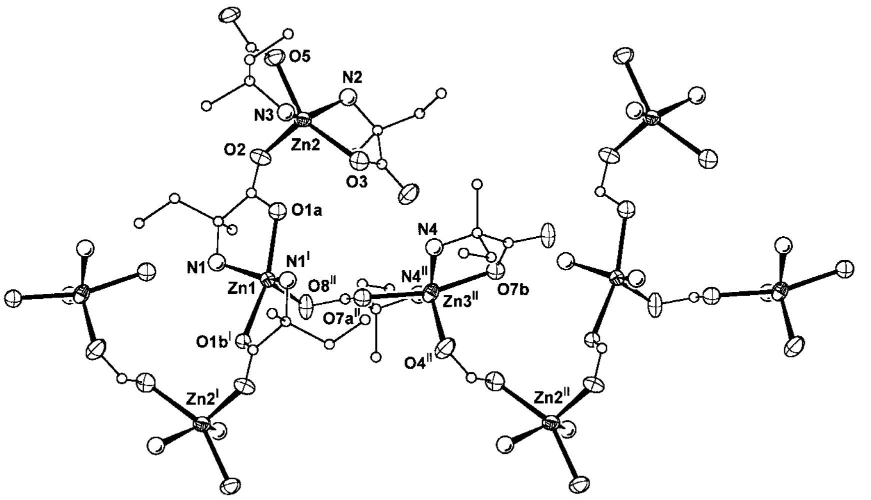


Figure 3. $Zn(iva)_2 \cdot 2H_2O$ (**4**): connectivity model leading to a one-dimensional coordination polymer. The polymer strand runs from left to right. Hydrogen atoms are omitted. For symmetry transformations see footnote in Table 1.

Crystals of $Zn(iva)_2 \cdot 2H_2O$ (**4**) are made up of carboxylate-bridged $\{Zn(iva)_2\}$ moieties and non-coordinating water molecules. The bridging is of the *syn-anti* type. Because Zn1 and Zn3 are disordered around centers of inversion,[37] the interpretation of the crystallographic data is partly ambiguous. One possible connectivity pattern leads to the infinite chain structure shown in Figure 3. Alternatively, Zn3 instead of $Zn3^{II}$ (for the symmetry transformation please see footnote in Table 1) may be linked to Zn1 via a carboxylate bridge. At the same time, Zn3 and Zn2 would be bridged. This results in a cyclic trimer and disruption of the chain (Figure 4). Although the connectivity is therefore not clear, the coordination spheres of the metal ions are well-defined. Each zinc ion is five-coordinate in an O_3N_2 environment. Selected bond lengths and angles are given in Table 1. The coordination polyhedra are slightly distorted square pyramidal (Zn2, $\tau = 0.18$) and intermediate between trigonal bipyramidal and square pyramidal (Zn1, $\tau = 0.43$; Zn3, $\tau = 0.45$).

$\{Zn(iva)_2\}$ moieties connected by *syn-anti*-carboxylate bridges also appear in crystalline $Zn(iva)_2 \cdot 3.25H_2O$ (**5**); the water molecules do not coordinate. Otherwise the structure of **5** differs strongly from that of **4**. Six $\{Zn(iva)_2\}$ moieties form the discrete cyclic complex $[Zn_6(iva)_{12}]$, which contains a puckered 24-membered $\{ZnOCO\}_6$ ring (Figure 5). A CSD search[28] revealed that the *cyclo*-$\{M(\mu\text{-carboxylato-}\kappa O{:}\kappa O')\}_6$ structural motif of **5** was previously unknown for M = Zn. Furthermore, there is only one α-amino acidato metal

Table 1. Bond lengths [Å] and angles [°] at the zinc atoms of $Zn(iva)_2 \cdot 2H_2O$ (**4**).[a]

Zn1–O1a	2.155(10)	Zn2–N2	2.037(6)
Zn1–O1b^I	2.158(8)	Zn2–N3	2.041(6)
Zn1–O8^{II}	2.123(5)	Zn3–O4	1.928(5)
Zn1–N1	1.881(6)	Zn3–O7a	2.128(9)
Zn1–N1^I	1.965(6)	Zn3–O7b^{II}	2.143(10)
Zn2–O2	1.967(5)	Zn3–N4	1.874(6)
Zn2–O3	2.194(5)	Zn3–N4^{II}	1.984(6)
Zn2–O5	2.107(5)		
O1a-Zn1-O1b^I	162.3(3)	O3-Zn2-N2	75.4(2)
O1a-Zn1-O8^{II}	103.8(3)	O3-Zn2-N3	96.1(2)
O1a-Zn1-N1	78.3(3)	O5-Zn2-N2	88.9(2)
O1a-Zn1-N1^I	94.1(3)	O5-Zn2-N3	78.6(2)
O1b^I-Zn1-O8^{II}	93.7(3)	N2-Zn2-N3	138.8(3)
O1b^I-Zn1-N1	95.4(3)	O4-Zn3-O7a	100.2(3)
O1b^I-Zn1-N1^I	79.0(3)	O4-Zn3-O7b^{II}	96.7(3)
O8^{II}-Zn1-N1	103.0(3)	O4-Zn3-N4	113.9(3)
O8^{II}-Zn1-N1^I	120.5(3)	O4-Zn3-N4^{II}	110.0(3)
N1-Zn1-N1^I	136.3(2)	O7a-Zn3-O7b^{II}	163.1(3)
O2-Zn2-O3	104.8(2)	O7a-Zn3-N4	78.3(3)
O2-Zn2-O5	105.1(2)	O7a-Zn3-N4^{II}	96.7(3)
O2-Zn2-N2	112.3(3)	O7b^{II}-Zn3-N4	93.8(3)
O2-Zn2-N3	108.8(2)	O7b^{II}-Zn3-N4^{II}	78.4(3)
O3-Zn2-O5	149.7(2)	N4-Zn3-N4^{II}	136.1(2)

[a] Symmetry transformations: (I): $1-x, 1-y, 2-z$; (II): $-x, 1-y, 2-z$.

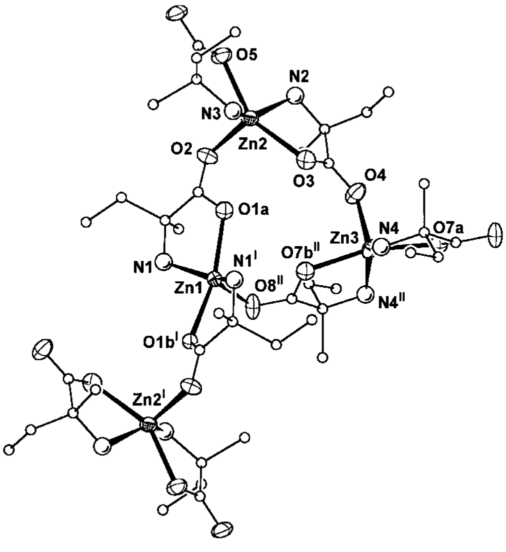


Figure 4. $Zn(iva)_2 \cdot 2H_2O$ (**4**): alternative connectivity model leading to a cyclic arrangement. Hydrogen atoms are omitted. For symmetry transformations see footnote in Table 1.

complex in which this motif was identified. This complex, namely $[Ni_6(pro)_{12}]$ ($pro^- =$ prolinate), does not exist as such, but was isolated with an additional incorporated metal ion (Sm^{3+} or $Eu^{2+/3+}$).[38] Its nickel ions are six-coordinate, whereas the zinc ions of **5** are five-coordinate. Thus **5** is unprecedented in the structural chemistry of metal α-amino acidates. The overall dimensions of the $[Zn_6(iva)_{12}]$ molecule are 2.1 × 1.1 nm. The O_3N_2 coordination polyhedron around Zn is a distorted square pyramid ($\tau = 0.27$, Figure 6). The isovalinato ligands in **5**, as in the other two structures described, are *O,N*-chelating and therefore participate in five-membered chelate rings.

Finally, the complexation behavior of α-aminoisobutyrate (aib^-) with zinc(II) is worth mentioning: the aib^- ligand, $(CH_3)_2C(NH_2)COO^-$, is formally derived from iva^- by replacing the ethyl with a second methyl group. Thus aib^- and iva^- are closely related to each other. Nevertheless, crystals of the zinc compound $Zn(aib)_2 \cdot 1.33H_2O$ are reported to contain mononuclear five- and six-coordinate complexes bearing coordinating water molecules;[39] this is in striking contrast to the situation found in the zinc isovalinate hydrates **4** and **5**.

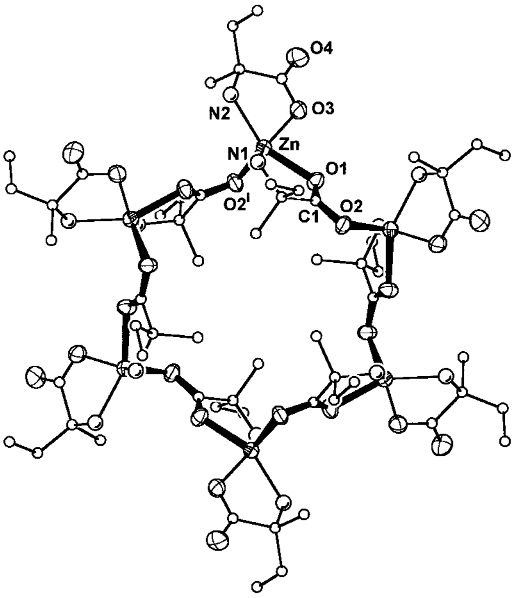


Figure 5. The *cyclo*-$[Zn_6(iva)_{12}]$ molecule in $Zn(iva)_2 \cdot 3.25H_2O$ (**5**). The $\{ZnOCO\}_6$ ring is highlighted. Hydrogen atoms are omitted. Symmetry transformation: (I): $-0.25 + y, 0.5 - z, 0.25 + x$.

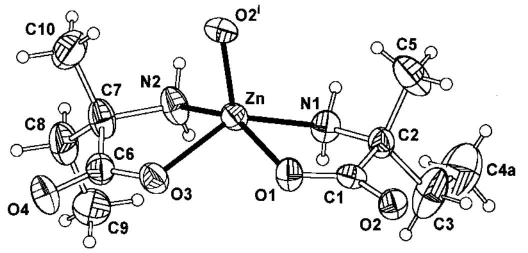
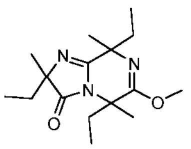


Figure 6. The coordination environment of the zinc atom in $Zn(iva)_2 \cdot 3.25H_2O$ (**5**). Displacement ellipsoids are shown at the 30% probability level. Bond lengths [Å] and angles [°]: Zn–O1 2.110(4), Zn–O2^I 1.990(4), Zn–O3 2.047(4), Zn–N1 2.052(5), Zn–N2 2.093(5), O1-Zn-O2^I 101.5(2), O1-Zn-O3 86.7(2), O1-Zn-N1 77.9(2), O1-Zn-N2 152.7(2), O2^I-Zn-O3 107.6(2), O2^I-Zn-N1 115.4(2), O2^I-Zn-N2 104.6(2), O3-Zn-N1 136.4(2), O3-Zn-N2 78.1(2), N1-Zn-N2 97.6(2). Symmetry transformation: (I): $-0.25 + y, 0.5 - z, 0.25 + x$.

Thermal transformations: The thermolysis and pyrolysis[40] of amino acids are of possible prebiotic relevance for two reasons. Firstly, the chemical compounds on early Earth were exposed to the thermal energy of volcanic activities and of episodical impacts of space bodies.[20b] Secondly, amino acids in meteorites, interplanetary dust particles, comets, and asteroids experienced more or less high temperatures on entering the Earth's atmosphere.[5, 41] Recently, Basiuk and coworkers have extensively studied the thermal transformations of solid α-amino acids with respect to these prebiotic aspects.[41, 42] They identified several mono-, di-, and tricyclic condensation products which were formed in the temperature range of 230–800 °C. Near the lower temperature limit, catalysts, such as silica gel and lava, were necessary; beyond the higher limit, neither the amino acids nor their condensation products survived. One problem with the thermal transformation of amino acids is the ease with which they sublime and thereby escape from high-temperature zones. Atmospheric movement at hot surfaces evidently assists this process. At normal pressure, the sublimation of simple α-amino acids usually starts well below 200 °C, for example, at 150–151 °C for isovaline[43] (see also the synthesis of isovaline in the Experimental Section). In contrast to isovaline and valine, their zinc and calcium salts are nonvolatile and thus can keep the acidates in places where temperatures are above the sublimation temperatures of the acids. In the following, we discuss preliminary results of thermolysis experiments on three selected metal amino acidates.

Solid samples of $Zn_3Cl_2(iva)_4$ (**1**), $Zn(val)_2$ (**3**) and $Ca(val)_2 \cdot H_2O$ (**8**) were heated to 320 °C in a slow nitrogen stream, as described in the Experimental Section. Within a few hours the compounds had decomposed to a large extent. Three groups of thermolysis products were found: i) a nonvolatile solid residue in the heating zone, ii) volatile products that were carried by the nitrogen stream to cooler parts of the apparatus where they condensed as liquids or solids, and iii) products that had a high vapor pressure at 0 °C (temperature of the cold trap) and therefore left the apparatus as gases. For all three starting materials, gas-chromatographic analyses of the liquid products alone revealed that *at least* 50–60 different compounds had formed from a single metal amino acidate! The majority of these compounds is still waiting for identification.

Crystalline **1** is thermally stable up to ≈300 °C. At slightly higher temperatures the crystals slowly decomposed without previous melting (see Experimental Section for details). When **1** was heated under EI mass-spectroscopic conditions, intense peaks at m/z 293 (45%) and 278 (100%) were observed. These peaks are assigned to M^+ and $[M - CH_3]^+$ of the heterocycle **9**. This heterocycle is derived from **10**, which is a condensation product of three isovaline molecules. Compounds analogous to **10** have been reported as thermolysis and pyrolysis products of the amino acids valine and α-aminoisobutyric acid by Basiuk et al.[41b, 41c, 42] Unlike **10**, heterocycle **9** is incapable of forming strong hydrogen bonds and thus should be more volatile and more easily observable in the mass spectrum. O-Methylation is assumed for **9** because in comparable compounds significant $[M - CH_3]^+$ peaks were observed only with O-, but not with N-methylation.[44] When **1** was thermolyzed at 320 °C in an N_2 stream (flow velocity: 40 cm min^{-1}), some simple decomposition products were identified, namely ethyl methyl ketone, CO_2, CO, H_2O, NH_3, and HCN. CO_2, H_2O, and NH_3 formed NH_4HCO_3. The observation that **1** can release CO, NH_3, and HCN is especially interesting because these gases have been used as starting materials for important, potentially prebiotic syntheses, of which the formation of the nucleic-acid base adenine from NH_4CN solutions is perhaps the most remarkable.[4a]



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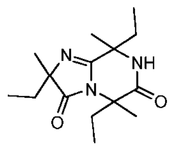

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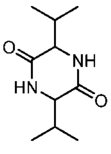
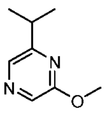


11

From the thermolysis of **3** (320 °C, velocity of N_2 flow: 3 cm min^{-1}) colorless needles of 3,6-diisopropylpiperazine-2,5-dione (**11**), the cyclic dipeptide of valine, were obtained. The mass of **11** that was isolated corresponded to 8% of the mass of **3** used in the experiment. As in the case of **1**, NH_4HCO_3 and CO were observed as thermolysis products. However, no significant amounts of HCN were detectable. Isobutylamine, the decarboxylation product of valine, was identified. The black thermolysis residue consisted of zinc oxide, as judged from a very strong, characteristically shaped IR band at $\tilde{\nu} = 440$ cm^{-1},[45] and of nonvolatile organic components.



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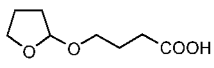

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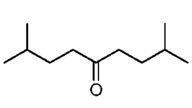

14

The thermolysis of **8**, under the same conditions as for **3**, also gave the cyclic dipeptide **11** as a major product (15% of the mass of **8** used). Other condensable products occurred at ≈22%, gases at ≈21%, and a nonvolatile residue at 42%. The compounds **12**–**14** were found among the condensed products. 2-Isopropyl-6-methoxypyrazine (**12**) was identified by GC/MS comparison with the commercially available 3-methoxy isomer, which showed a nearly identical EI mass spectrum; however it had a clearly different gas-chromatographic retention time. The possibility that the observed compound is the 5-methoxy isomer cannot be ruled out, although this seems less probable because the formation of this isomer from **11** would require the migration of one of the ring substituents, whereas the formation of **12** from **11** would be more straightforward. The compounds **13** and **14** were identified by combined mass spectrometric and ^1H and ^{13}C NMR spectroscopic methods. Acid **13** is the condensation product of 4-hydroxybutanal and 4-hydroxybutanoic acid. The existence of **14** as a thermolysis product is intriguing because it demonstrates that chains of at least nine carbon atoms can form from valinate. Sufficiently long carbon chains are regarded as prerequisite to the prebiotic self-organization of membranes, vesicles, and primitive cellular systems.[46] The light-brown thermolysis residue of **8** consisted of calcite (≈74%) and nonvolatile organic compounds, as inferred from analyses (C, H, Ca, CO_3^{2-}, N), IR spectra, and powder

X-ray diffraction patterns.[47] The organic constituents partly dissolved in boiling water. This extractable portion of the residue contained isopropyl groups and carboxyl and/or carboxylate groups. However, no valinate was present. Therefore, the calcium amino acidate had been completely thermally transformed.

Conclusions

The following are the principle results and conclusions of this work: i) It is proposed that zinc and calcium complexes of abiotically formed racemic α-amino acidates, for example, *rac*-valinate and *rac*-isovalinate, might have existed on the early Earth. Necessary assumptions concerning the prebiotic conditions are within the framework of current geochemical and cosmochemical models. ii) In the laboratory, these complexes readily form from simple metal compounds, such as $ZnCl_2$, ZnO, $Zn(OH)_2$, and $Ca(OH)_2$ along with the respective amino acid in aqueous solutions. The zinc(II)/isovalinate system shows an unexpected compositional and structural diversity. Here, at least four compounds can be isolated, namely $Zn_3Cl_2(iva)_4$ (**1**), $Zn(iva)_2 \cdot 2H_2O$ (**4**), $Zn(iva)_2 \cdot 3.25H_2O$ (**5**), and $Zn(iva)_2$ (**6**). The crystal structures of **1**, **4**, and **5** differ from each other rather strongly. One of the few common features is the presence of bridging isovalinato ligands. iii) Thermolyses of solid **1**, $Zn(val)_2$ (**3**), and $Ca(val)_2 \cdot H_2O$ (**8**) at 320 °C in an N_2 stream yielded a surprising number of organic products. The α-amino acidates are not only thermally degraded, but are also transformed into larger molecules with new functional groups. A variety of reactions occur, for example, C–C bond breaking and bond formation. Some of these reactions are probably catalyzed by the metal ions acting as Lewis acids. Thermal transformations of metal amino acidates might thus have contributed to the prebiotic chemical inventory on the early Earth.

Experimental Section

Instrumentation: IR spectra (KBr pellets) were obtained on a Bio-Rad FTS 7PC spectrometer. Only the ≈15 strongest IR bands are listed for each compound. $^{13}C\{^1H\}$ NMR spectra (75.5 MHz, D_2O) were recorded at ambient temperature on a Bruker AM 300 spectrometer. 1,4-Dioxan served as the internal standard ($\delta_c = 67.19$[48]). Mass spectra were measured with Finnigan-MAT 212 and Finnigan-MAT 95 instruments. A Philips PW 1050/80 automated powder diffractometer ($Cu_{K\alpha}$ radiation) and a STOE IPDS area detector diffractometer ($Mo_{K\alpha}$ radiation) were used to obtain diffraction data of polycrystalline samples. The decomposition temperatures were determined in unsealed melting-point capillaries. Elemental analyses were performed by the Mikroanalytisches Labor Beller, Göttingen; Analytische Laboratorien Malissa und Reuter, Lindlar; and Mikroanalytisches Labor Pascher, Remagen (Germany). Some of the C/H/N analyses were obtained with a Fisons Instruments EA 1108 elemental analyzer at our central analytical department.

Starting materials: Racemic isovaline (Hiva) was obtained from ethyl methyl ketone by the Strecker synthesis.[49] The final step, namely the dehydration of Hiva · H_2O, was accomplished by vacuum sublimation at ≈160 °C. Spectroscopic data of Hiva (see also ref. [27, 50]): IR: $\tilde{\nu} = 3600–2300$ (s, br) 2972 (w), 2562 (w, br), 2066 (w, br), 1605 (vs, br), 1460 (m), 1404 (s), 1368 (m), 1339 (m), 1296 (s), 1181 (m), 891 (m), 802 (s), 586 (s), 538 (s), 401 cm^{-1} (s); ^{13}C NMR: $\delta = 8.3, 22.7, 31.1, 62.4, 176.5$; ^{13}C NMR spectrum of isovalinate (iva^-, 0.20 M solution prepared in situ from equimolar amounts of Hiva and NMe_4OH): $\delta = 8.8, 26.2, 34.1, 59.5, 185.7$.

ε-Zinc hydroxide was prepared as described in the literature.[51] Deionized water was used throughout. All other chemicals, including racemic valine (Hval; Fluka, ≥99.0%), were purchased commercially and used without further purification. ^{13}C NMR spectrum of valinate (val^-, 0.20 M solution prepared in situ from equimolar amounts of Hval and NMe_4OH): $\delta = 17.3, 19.7, 32.3, 62.5, 183.6$.

Preparation of $Zn_3Cl_2(iva)_4$ (1): A solution of $ZnCl_2$ (2.04 g, 15.0 mmol), Hiva (3.51 g, 30.0 mmol), and urea (0.90 g, 15.0 mmol) in water (60 mL) was kept at 80 °C for 9 d (CO_2 evolution!). During this period, colorless crystals of **1** formed; these were collected on a large-pored glass filter, thoroughly washed with water, and dried in a vacuum. The filtrate was concentrated to a volume of 45 mL and kept at 80 °C. After 5 d a second crop of crystals was isolated. Total yield: 2.86 g (78%). Thermal behavior: crystals started turning brown at ≈310 °C; at ≈320 °C gas evolution and slow formation of a dark-brown melt were observed. IR: $\tilde{\nu} = 3283$ (s), 3239 (m), 1643 (vs), 1593 (s), 1464 (m), 1385 (s), 1290 (s), 1200 (s), 1090 (s), 1051 (s), 816 (s), 760 (m), 683 (s), 392 (m), 305 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{40}Cl_2N_4O_8Zn_3$ (731.6): C 32.83, H 5.51, Cl 9.69, N 7.66, Zn 26.81; found C 32.91, H 5.53, Cl 9.80, N 7.29, Zn 26.76.

Preparation of $Zn_3Cl_2(val)_4$ (2): A solution of $ZnCl_2$ (1.64 g, 12.0 mmol), Hval (1.87 g, 16.0 mmol), urea (0.48 g, 8.0 mmol), and NaCl (2.81 g, 48.0 mmol) in water (30 mL) was kept at 80 °C for 9 d (CO_2 evolution!). The colorless crystalline product was isolated on a large-pored glass filter, thoroughly washed with water, and dried in a vacuum. Yield: 1.28 g (44%); IR: $\tilde{\nu} = 3289$ (s), 3252 (s), 1640 (vs), 1595 (s), 1375 (s), 1323 (m), 1102 (s, br), 1015 (m), 795 (s), 650 (s), 565 (m), 374 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{40}Cl_2N_4O_8Zn_3$ (731.6): C 32.83, H 5.51, Cl 9.69, N 7.66, Zn 26.81; found C 33.33, H 5.51, Cl 9.56, N 7.61, Zn 26.80.

Preparation of $Zn(val)_2$ (3)

Method A: A solution of $ZnCl_2$ (1.36 g, 10.0 mmol), Hval (3.51 g, 30.0 mmol), and urea (0.90 g, 15.0 mmol) in water (40 mL) was kept at 80 °C for 15 d (CO_2 evolution!). Colorless crystals of **3** were collected on a large-pored glass filter. Keeping the filtrate at 80 °C for additional 7 d yielded a second crop of crystals. The product was thoroughly washed with water and dried in a vacuum. Total yield: 2.81 g (94%); IR: $\tilde{\nu} = 3306$ (m), 3250 (m), 2961 (m), 1604 (vs), 1564 (vs), 1431 (m), 1325 (s), 1142 (s), 1123 (s), 1090 (s), 1051 (m), 785 (s), 708 (m), 577 cm^{-1} (m); elemental analysis calcd (%) for $C_{10}H_{20}N_2O_4Zn$ (297.7): C 40.35, H 6.77, N 9.41, Zn 21.97; found C 40.48, H 6.67, N 9.23, Zn 21.92.

Method B: A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (5.95 g, 20.0 mmol), Hval (4.69 g, 40.0 mmol), and urea (1.20 g, 20.0 mmol) in water (60 mL) was kept at 80 °C for 15 d (CO_2 evolution!). The crystalline product was collected on a large-pored glass filter. The filtrate was kept at 80 °C for additional 13 d, and a second crop of crystals was isolated. The crystals were thoroughly washed with water and dried in a vacuum. Total yield: 3.57 g (60%). The IR spectrum was identical to that of the product prepared by Method A. Elemental analysis calcd (%) for $C_{10}H_{20}N_2O_4Zn$ (297.7): C 40.35, H 6.77, N 9.41, Zn 21.97; found C 40.36, H 6.85, N 9.37, Zn 21.91.

Preparation of $Zn(iva)_2 \cdot 2H_2O$ (4)

Method A: ZnO (2.44 g, 30.0 mmol) was added to a solution of Hiva (1.76 g, 15.0 mmol) in water (20 mL). The reaction mixture was heated under reflux for 14 d and then filtered hot to remove unreacted ZnO. The filtrate was kept at 1 °C, after its volume had been reduced by a few mL. After 3 d, a small amount of cube-shaped crystals of **5** was removed by filtration and discarded. The filtrate was slightly concentrated by evaporation and stored at room temperature. Needle- or diamond-shaped crystals of **4** formed, which were isolated on a glass filter and dried between filter papers for a short time. Yield: 0.17 g (7%); IR: $\tilde{\nu} = \approx 3480$ (m, br), 3267 (s), 2971 (m), 1630 (vs, sh), 1574 (vs), 1464 (s), 1416 (s), 1395 (s), 1296 (m), 1186 (s), 1080 (m), 1051 (m), 934 (m), 814 (m), 611 cm^{-1} (s); elemental analysis calcd (%) for $C_{10}H_{24}N_2O_6Zn$ (333.7): C 35.99, H 7.25, N 8.40, Zn 19.60; found C 35.92, H 7.58, N 8.37, Zn 19.75.

Method B: ε-$Zn(OH)_2$ (1.59 g, 16.0 mmol) was added to a solution of Hiva (1.87 g, 16.0 mmol) in water (20 mL). The reaction mixture was heated under reflux for 4 d and then filtered hot to remove unreacted $Zn(OH)_2$. The filtrate was slightly concentrated by evaporation and stored at 1 °C. After 1 d, a small amount of elongated diamond-shaped crystals of **4** had formed, one of which was used for the single-crystal X-ray structure determination.

Preparation of Zn(iva)$_2$·3.25H$_2$O (5) and Zn(iva)$_2$ (6): ZnO (2.44 g, 30.0 mmol) was added to a solution of Hiva (1.76 g, 15.0 mmol) in water (20 mL). The reaction mixture was heated under reflux for 14 d and then filtered hot to remove unreacted ZnO. The volume of the filtrate was then reduced by a few mL. On standing at 1 °C, cube-shaped crystals of **5** formed within 20 d. They were isolated and liberated from adhering mother liquor with filter paper. These crystals, however, could not be stored because they effloresced very rapidly. Therefore, they were transformed into the completely dehydrated form **6** in a vacuum (oil pump) for 4 h. Yield: 0.19 g (9 %); IR: $\tilde{\nu} = 3441$ (m), 3275 (s), 2972 (m), 1620 (vs, sh), 1568 (vs), 1464 (s), 1416 (s), 1397 (s), 1294 (m), 1184 (m), 1072 (m), 1047 (m), 934 (m), 815 (m), 610 cm^{-1} (m); ^{13}C NMR (0.20 M solution): $\delta = 8.3$, 24.7, 32.4, 60.7, 182.2; elemental analysis calcd (%) for $C_{10}H_{20}N_2O_4Zn$ (297.7): C 40.35, H 6.77, N 9.41, Zn 21.97; found C 40.62, H 7.01, N 9.27, Zn 21.82.

Preparation of Ca(iva)$_2$·xH$_2$O (7): Ca(OH)$_2$ (1.48 g, 20.0 mmol) was added to a solution of Hiva (2.34 g, 20.0 mmol) in water (20 mL). The reaction mixture was heated under reflux for 3 d and then filtered hot to remove unreacted Ca(OH)$_2$. The volume of the filtrate was reduced to ≈7 mL by rotary evaporation. On standing at room temperature for several days, a white crystalline precipitate of **7** formed which was collected on a glass filter and dried in a vacuum. Yield: 1.40 g (50 % for $x = 0.5$). Thermal behavior: when a sample of the precipitate was heated, a liquid (probably water) was lost and the glassy residue turned into a brown melt at ≈316 °C; IR: $\tilde{\nu} = 3359$ (m), 3262 (m), 2965 (s), 1626 (vs, sh), 1597 (vs), 1462 (s), 1398 (s), 1292 (m), 1202 (m), 999 (m), 953 (m), 926 (s), 885 (m), 808 (s), 596 cm^{-1} (m); ^{13}C NMR (0.10 M solution): $\delta = 8.7$, 26.2, 34.1, 59.6, 185.9; elemental analysis calcd (%) for $C_{10}H_{21}CaN_2O_{4.5}$ (281.4, $x = 0.5$): C 42.69, H 7.52, Ca 14.24, N 9.96; found C 43.12, H 7.65, Ca 13.80, N 10.08.

Preparation of Ca(val)$_2$·H$_2$O (8): Ca(OH)$_2$ (1.48 g, 20.0 mmol) was added to a solution of Hval (2.34 g, 20.0 mmol) in water (20 mL). The reaction mixture was heated under reflux for 6 h and then filtered hot to remove unreacted Ca(OH)$_2$. The volume of the filtrate was reduced by rotary evaporation until precipitation occurred. The white crystalline solid was collected on a glass filter, washed with a 1:1 (v/v) water/methanol mixture, and dried in a vacuum. Yield: 0.85 g (29 %). Thermal behavior: gas evolution slowly started at ≈295 °C; the resulting glassy mass slowly turned light-brown at ≈302 °C; brown and colorless droplets formed in the upper part of the capillary. IR: $\tilde{\nu} = 3352$ (m), 3287 (m), 3202 (m, br), 2955 (s), 1624 (s, sh), 1566 (vs), 1422 (s), 1366 (s), 1011 (s), 932 (s), 839 (m), 766 (m), 648 (m), 598 cm^{-1} (m); ^{13}C NMR (0.10 M solution): $\delta = 17.2$, 19.6, 32.2, 62.4, 183.6; elemental analysis calcd (%) for $C_{10}H_{22}CaN_2O_5$ (290.4): C 41.36, H 7.64, Ca 13.80, N 9.65; found C 41.11, H 7.48, Ca 13.10, N 9.33.

X-ray crystallography: Crystal data and details of the data collection and structure refinement are summarized in Table 2. Suitable single crystals of **1**, **4**, and **5** were obtained from syntheses identical with or very similar to those described above. The crystals were sealed into thin-walled glass capillaries and mounted on a Siemens/STOE AED2 diffractometer. Graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used. Accurate lattice parameters and their standard deviations were determined by a least-squares fit to the angular settings of typically 50 automatically centered reflections. The intensity data were collected at 23 ± 1 °C. The $\omega - 2\Theta$ (for **1** and **4**) and the ω step scan technique (for **5**) were used. Three check reflections were measured every 45 min. There was no significant decay of the crystals. For **1** and **5** empirical absorption corrections (ψ scans) were applied to the data; min. and max. transmissions were 0.2114, 0.4247 for **1** and 0.2416, 0.3247 for **5**. The structures were solved by direct methods and refined on F^2 values. The programs SHELXTL PLUS,[52] SHELXTL PC,[53] SHELXL-93,[54] SHELXL-97,[55] and DIAMOND[56] were used.

Compound 1: The structure was successfully refined in the noncentrosymmetric space group $P\bar{4}b2$. The absolute structure parameter was −0.02(3) for the final model. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were included on idealized positions.

Compound 4: Zn1 and Zn3 are disordered around inversion centers. Anisotropic displacement parameters were applied to the non-hydrogen atoms, except O1, O7, C4, and C19 which are each disordered on two positions. C4 and C19 are γ-carbon atoms, that is they belong to methyl groups of ethyl sidechains. Their disorders at the β-carbon atoms are interpreted as the presence of both enantiomers at the respective ligand site. The hydrogen atoms on the C and N atoms were assigned to calculated positions, while the hydrogen atoms of the water molecules were localized from difference maps and included by use of a riding model.

Compound 5: Anisotropic thermal parameters were refined for the non-hydrogen atoms, except C4, which shows the same type of disorder as the carbon atoms C4 and C19 of **4** (see above). On account of special positions or disorder of the water oxygen atoms, some of the water molecules were left without hydrogen atoms. The others were refined with hydrogen atoms in the riding mode; the initial positions of the hydrogen atoms were taken from difference maps. Hydrogen atoms were added geometrically to C and N atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148127 (**1**), CCDC-148128 (**4**), and CCDC-148129 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Thermolysis experiments: Compounds **1**, **3**, or **8** (1 to 40 g) were exactly weighed out and transferred to a quartz-glass boat. The larger amounts of metal amino acidates that were required in some experiments were obtained by scaling up the synthetic procedures given above. The quartz-glass boat was positioned in a glass tube which had been placed into a tube furnace. A slow stream of nitrogen gas was passed through the tube, initially at room temperature to purge the apparatus from oxygen and later during the thermolysis. The temper-

Table 2. Crystallographic data and details of the data collection and structure refinement for compounds **1**, **4**, and **5**.

	1	**4**	**5**
formula	$C_{20}H_{40}Cl_2N_4O_8Zn_3$	$C_{10}H_{24}N_2O_6Zn$	$C_{60}H_{159}N_{12}O_{43.5}Zn_6$[a]
M_r	731.6	333.7	2137.3[a]
crystal system	tetragonal	monoclinic	cubic
space group	$P\bar{4}b2$ (no. 117)	$P2_1/c$ (no. 14)	$Fd\bar{3}$ (no. 203)
a [Å]	11.114(2)	10.991(1)	34.424(5)
b [Å]	–	24.342(4)	–
c [Å]	11.528(1)	12.352(2)	–
β [°]	–	112.81(1)	–
V [Å^3]	1424.0(4)	3046.2(8)	40793(10)
Z	2	8	16[a]
ρ_{calcd} [g cm^{-3}]	1.706	1.455	1.392
μ(Mo$_{K\alpha}$) [cm^{-1}]	27.43	16.35	14.75
crystal size [mm]	0.87 × 0.57 × 0.08	0.42 × 0.19 × 0.11	0.72 × 0.61 × 0.34
2Θ range [°]	3.5–53.9	3.3–46.1	3.3–46.0
reflections collected	1627	4443	4774
independent reflections (R_{int})	1554 (0.0364)	4193 (0.0603)	2389 (0.0772)
reflections used in final refinement	1554	4193	2387
parameters	85	348	195
$R1$ [$I > 2\sigma(I)$]	0.0366	0.0606	0.0540
$wR2$ (all data)	0.0866	0.1396	0.1407
goodness-of-fit (on F^2)	1.056	1.048	1.039
largest difference peak/hole [e Å^{-3}]	+0.76/−0.40	+0.44/−0.33	+0.49/−0.23

[a] Refers to the hexamer.

ature of the heating zone of the furnace was raised from room temperature to 320 °C within a few minutes and kept there for the next 4 h (**1**, **3**) and 7 h (**8**), respectively. At the gas-outlet end, the tube protruded from the furnace and was equipped with an array of hollows and a cold trap, which allowed the preseparation of thermolysis products transported by the carrier gas. Further separations of the condensed products were achieved by standard HPLC, GC, and preparative column techniques. Gaseous products were selectively identified with Dräger Tubes (Dräger Sicherheitstechnik GmbH, Lübeck (Germany)).

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