High Nuclearity $Zn^{II}/MeCO_2^-/(C_5NH_4)_2CO_2^{2-}$ Clusters by "Depolymerization": Conversion of a Three-Dimensional Coordination Polymer Containing Hexameric Units into Its Constituent Hexanuclear Complex[**]

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One of the goals in polynuclear coordination chemistry is to control the nature of the final product and to escape from the reliance on spontaneous self-assembly. The elegant research of some groups,[1] which include those of Christou (coupling or linking smaller manganese fragments to make larger assemblies)[2] and Winpenny (oligomerizing low nuclearity clusters by desolvation),[3] supplied rare examples of such designed syntheses. In most cases, the precise nuclearity and structure of the reaction products could not be predicted from the reagents and synthetic conditions employed, even though the reactions were certainly directed toward the formation of higher nuclearity species. All these syntheses of higher nuclearity clusters used either covalent linking of lower nuclearity complexes or aggregation of "building blocks". An alternative attractive approach would be the cleavage, in a controlled manner, of coordination polymers $(M_x)_n$ containing recognizable high nuclearity M_x units ("polymers of clusters" or "polymers of aggregates") to obtain the discrete M_x clusters. Herein, we report our successful realization of this idea for $M = Zn^{II}$ and $x = 6$. The cleavage of coordination polymers into *mononuclear* complexes by donor solvents is well-known in inorganic chemistry.[4]

The reaction of $Zn(O_2CMe)_2 \cdot 2H_2O$ with di-2-pyridyl ketone, $(C_5NH_4)_2CO$, in a 3:1 molar ratio led to a colorless solution, from which the three-dimensional (3D) polymeric complex **1** containing doubly deprotonated anions of the *gem*-diol form $(C_5NH_4)_2C(OH)_2$ as ligands could be isolated; the presence of dianions is a consequence of the high $MeCO_2^-$ to $(C_5NH_4)_2C(OH)_2$ ratio (6:1) used in the reaction. The X-ray crystal structure analysis of **1** revealed repeating hexameric units (Figure 1)[5]; there is a twofold axis passing through C6 and C26. Each cluster unit has two $\mu_4{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1$ $(C_5NH_4)_2CO_2^{2-}$ dianions (**A**), six *syn,syn*-$\mu_2{:}\eta^1{:}\eta^1$ $MeCO_2^-$ ions and two *syn,anti*-$\mu_2{:}\eta^1{:}\eta^1$ $MeCO_2^-$ ions as ligands; the latter provide the intercluster covalent linking. Inspired by the remarkable structure of **1** and considering the Zn⋯Zn distances of less than 3.7 Å, we refer to the cluster unit as a "twin anchor" (**B**). To the best of our knowledge, **1** is only the second example of a zinc(II) polymer containing hexameric repeating units; the other example is $[\{(ZnCl)_6(\mu_2\text{-}Cl)_8\}^{2-}]_n$, which was isolated with $[(\eta\text{-}C_5Me_5)_3Nb_3Cl_3O_3]^+$ as the counterion.[6]

$[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8]_n$ **1**

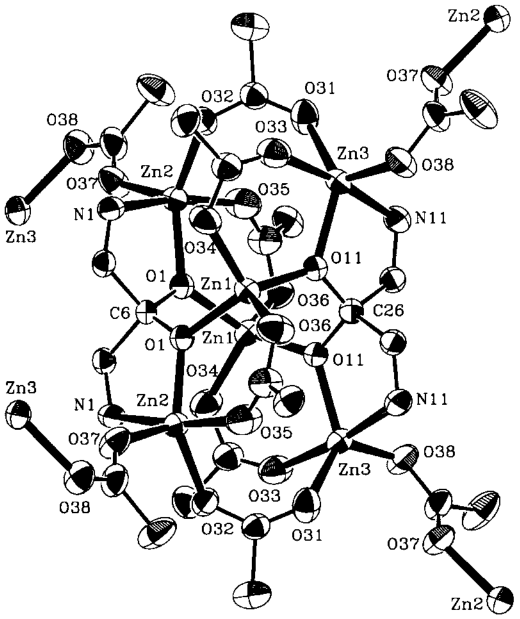
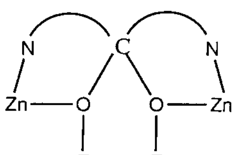


Figure 1. A portion of the 3D polymeric structure of **1** showing one $[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8]$ cluster unit, four extra Zn^{II} atoms belonging to four different units (peripheral Zn2, Zn2, Zn3, Zn3) and two extra *syn,anti*-$\mu_2{:}\eta^1{:}\eta^1$ acetate ligands; the extra metal ions and acetate ligands have been drawn to emphasize the intercluster connections. Atoms generated symetrically by the twofold axis that runs through C6 and C26 are identically labeled. Most of the carbon atoms of the pyridine rings have been omitted. Intracluster distances [Å]: Zn⋯Zn 3.38–6.56, Zn-O 1.92–2.12, Zn-N 2.11–2.13. The intercluster distance Zn2⋯Zn3 is 5.014(1) Å. The open lines indicate weak bonds (2.50–2.75 Å).



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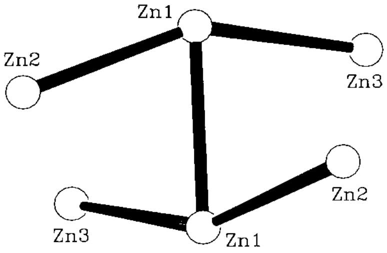

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The presence of well-defined Zn$_6$ cluster units in **1** suggested that solvation, that is, reaction with terminal donor solvent molecules, might cause polymer cleavage and formation of the constituent hexanuclear complex. Since the hexanuclear units in **1** are connected by the four metal ions Zn2, Zn3, and their symmetry partners, we reasoned that these sites might be suitable for the attachment of donor solvent molecules, which has, indeed, turned out to be the case. Treatment of a slurry of **1** in MeCN with MeOH and few drops of H_2O led to a homogeneous solution, from which the discrete hexanuclear cluster **2** slowly crystallized in good yield. The purity of the bulk material **1** used to form **2** was confirmed by comparison of the observed and calculated X-ray powder diffraction (XRPD) patterns.

$[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8(H_2O)_2]\cdot 3.5\,H_2O\cdot 0.76\,MeCN$ **2**

Complex **2** (Figure 2)[5] has no symmetry elements and is held together by two terminal aqua ligands, two asymmetrically chelating $MeCO_2^-$ ions, four *syn,syn*-$\mu_2{:}\eta^1{:}\eta^1$ $MeCO_2^-$ ions, two $\mu_2{:}\eta^1{:}\eta^2$ acetate ions and two $(C_5NH_4)_2CO_2^{2-}$ dianions, which also adopt (as in **1**) the coordination mode $\mu_4{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1$ (**A**); this coordination mode is very rare and has been observed only in a dodecanuclear copper(II) cluster.[7a] The six Zn^{II} atoms of **2** adopt the same topological arrangement **B** found in **1**. The hexanuclear molecules are connected through a complex system of intermolecular hydrogen bonds involving both the aqua ligands, all the lattice molecules, and the acetate oxygen atoms O25, O29, O30, O35, and O36. Complex **2** is the sixth structurally characterized member of a group of polynuclear 3d metal complexes with mixed $(C_5NH_4)_2CO_2^{2-}/RCO_2^-$ ligation, the other examples being Cu$^{II}_7$,[7a] Cu$^{II}_{12}$,[7a] and Co$^{II}_9$[7b,c] clusters, and it is only the second example of a discrete hexanuclear Zn^{II} species with exclusively O and/or N ligation.[8]

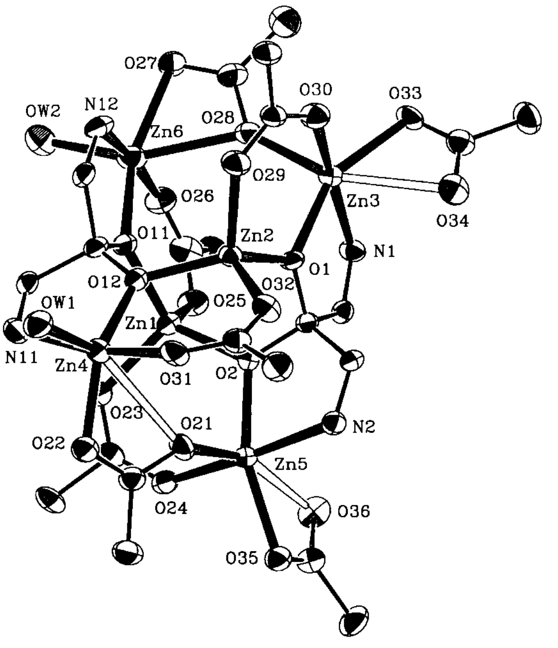
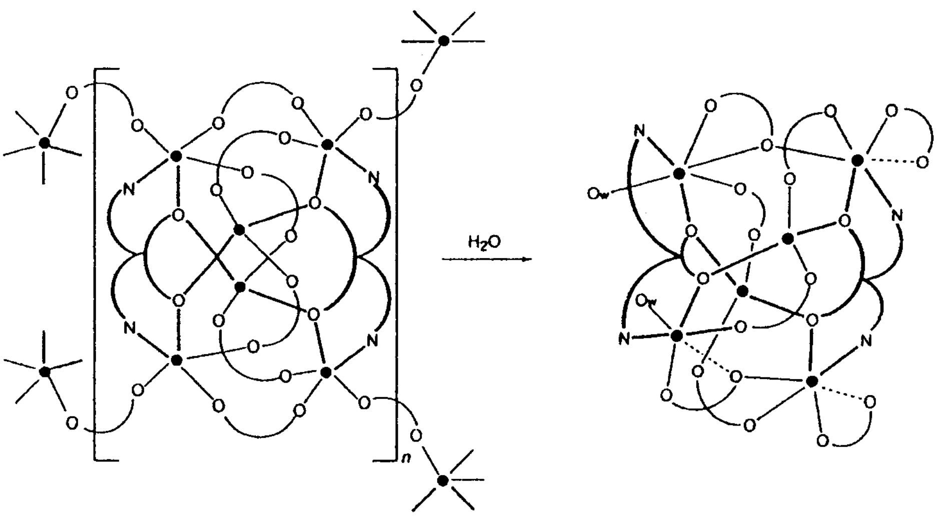


Figure 2. Molecular structure of **2**. Solvent molecules in the lattice are omitted. Most of the carbon atoms of the pyridine rings have been omitted for clarity. Interatomic distances [Å]: Zn ··· Zn 3.39–6.66, Zn-O 1.91–2.75, Zn-N 2.10–2.12.

The conversion of **1** into **2** [Eq. (1)] can be rationalized as follows: coordination of two H_2O molecules cleaves the polymer at two Zn^{II} sites per repeating unit; these sites are converted into six-coordinate ones by two new intracluster linkages (Zn6–O28 and Zn4 ··· O21 in **2**); the two remaining monodentate acetate ligands (formerly *syn,anti*-$\mu_2{:}\eta^1{:}\eta^1$) at the other two, formerly 5-coordinate, Zn^{II} sites become chelating. Thus, the four metal sites from which polymerization could start are coordinatively saturated (six-coordinate) in **2**, which contributes to the stability of the hexanuclear cluster.



(1)

The conversion of **1** into its constituent Zn$_6$ cluster does not depend on the volume ratio of the donor solvents H_2O and MeOH. Thus, dissolution of **1** in H_2O and addition of few drops of MeOH also led to a homogeneous solution from which the discrete cluster $[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8(H_2O)_2]\cdot 7\,H_2O\cdot MeOH$ crystallized. Single-crystal X-ray diffraction revealed[9] that the hexanuclear molecule of this complex is essentially superimposable on that of **2**, the only difference being the nature of the lattice molecules. Moreover, it appears that the $(Zn_6)_n \rightarrow Zn_6$ conversion is not limited by the nature of the donor solvent. For example, dissolution of **1** in the minimum volume of DMF and addition of Et_2O yielded a microcrystalline solid that, according to elemental analyses, IR spectroscopy, and thermal techniques (TG/DTA, DTA), can be formulated as $[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8(DMF)_2]\cdot 2\,DMF\cdot 0.5\,H_2O$.

Apart from the above-mentioned structural changes (coordination of H_2O molecules and formation of the Zn3–O34, Zn5–O36, Zn4–O21, and Zn6–O28 bonds in **2**), the

$[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8(H_2O)_2]$ molecules of **2** and the $[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8]$ cluster units in **1** are essentially identical with respect to their formulation, gross stuctural arrangement, and the coordination mode of the $(C_5NH_4)_2CO_2^{2-}$ ions.

The utility of our "depolymerization" approach is shown by the fact that direct reaction between three equivalents of $Zn(O_2CMe)_2 \cdot 2H_2O$ and one equivalent of $(C_5NH_4)_2CO$ in MeOH or MeOH/H_2O gave a mixture of **2**, $[Zn_4\{(C_5NH_4)_2C(OH)O\}_4(O_2CMe)_3(H_2O)] \cdot (MeCO_2) \cdot 7.5H_2O$[9] (the identity of this cubane cluster has been established by single-crystal X-ray diffraction), and an as-yet unidentified product.

The depolymerization procedure described above can be monitored by solid-state ^{13}C NMR spectroscopy; we[10a] and others[10b,c] have shown that this form of spectroscopy is an important complementary technique to X-ray crystallography for diamagnetic carboxylatometal complexes. The high-resolution solid-state ^{13}C NMR spectum of **1** (recorded at 75.5 MHz) contains four signals for both the methyl ($\delta = 24.40-21.51$) and the carboxylate carbon atoms ($\delta = 181.78-177.26$); this is consistent with the four crystallographically independent acetate ions present in the unit cell. The corresponding regions in **2** ($\delta = 24.31-20.53$, $184.55-175.20$) are more complicated, reflecting the presence of eight crystallographically inequivalent acetate ions. It might be suggested that the signals at $\delta = 184.55$ in the carboxylate region and at $\delta = 20.53$ in the methyl region, which are not present in the spectrum of **1**, belong to the two *asymmetrically* chelating acetate ligands; this deshielding effect has been interpreted in terms of an increased polarization of the carboxylate bond which makes the carbon atom more positive.[10c]

The present work represents a successful "test of feasibility" for our depolymerization approach, and the described procedure may be generally applicable because coordination polymers containing high nuclearity repeating units are not rare.[11] We recognize that the formation of **2** from **1** relies on the acetate ligand and its flexibility in converting from *syn,anti*-μ_2:η^1:η^1 into chelating (η^2) and from *syn,syn*-μ_2:η^1:η^1 into μ_2:η^1:η^2 coordination. Although there was no chance to predict the exact formula of the product (for example, the reaction could have given $[Zn_6\{(C_5NH_4)_2CO_2\}_2(O_2CMe)_8(H_2O)_4]$ with monodentate instead of chelating acetate ligands) and the precise form of the intracluster linkage, we are encouraged by the fact that it was possible to isolate a hexanuclear cluster without significantly altering the structure of the hexameric repeating unit of the polymer.

Three years ago, Ranford et al.[12a] reported the irreversible dehydration of discrete dinuclear zinc(II) complexes stabilized by noncovalent hydrogen bonds, which led to the construction of a 3D covalent polymer with the same basic architecture; their approach, which has been highlighted by Zaworotko,[12b] may be regarded as the opposite of the approach described here. Recently Yaghi et al. employed the concept of secondary building units (SBUs),[13] often used by zeolite chemists, for the design of highly porous and robust metal–organic carboxylate frameworks. SBUs are molecular clusters with ligand coordination modes and metal coordination environments which can be utilized in their transformation into extended crystalline porous networks using polytopic linkers. In a sense, if one follows Yaghi's approach, complex **2** is the SBU for **1**. Preliminary experiments, supported by TG/DTG, DTA, and XRPD data, revealed that **2** can be converted into **1** by heating.

Experimental Section

1: Solid $Zn(O_2CMe)_2 \cdot 2H_2O$ (0.66 g, 3.0 mmol) was dissolved under gentle reflux in a stirred solution of $(C_5NH_4)_2CO$ (0.18 g, 1.0 mmol) in MeCN (30 mL). Slow evaporation of the solvent from the resulting solution at room temperature gave colorless crystals of **1**, suitable for X-ray crystallography. The crystals were collected by filtration, washed with cold EtOH (2 × 5 mL) and Et_2O (2 × 5 mL), and dried in air, yield 80%; elemental analysis calcd for $C_{38}H_{40}N_4O_{20}Zn$ (%): C 36.1, H 3.2, N 4.4, Zn 31.0; found: C 36.2, H 3.4, N 4.3, Zn 30.8.

2: A slurry of **1** (0.25 g, 0.2 mmol) in MeCN (15 mL) was treated with a mixture of MeOH (6 mL) and H_2O (0.6 mL). The solid polymer dissolved rapidly. The solution was allowed to slowly concentrate by evaporation at room temperature to give colorless crystals, suitable for X-ray crystallography, which were collected by filtration, washed with a little cold EtOH and Et_2O, and dried in air; the formulation **2** was determined crystallographically, but the dried solid was analyzed as MeCN-free, yield 40%; elemental analysis calcd for $C_{38}H_{51}N_4O_{25.5}Zn_6$ (%): C 33.4, H 3.8, N 4.1, Zn 28.8; found: C 33.2, H 3.9, N 4.1, Zn 29.4.

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[5] Crystal data for **1**: Crystal dimensions 0.10 × 0.20 × 0.30 mm, orthorhombic, space group *Fdd*2, $a = 16.627(1)$, $b = 27.141(2)$, $c = 28.356(2)$ Å, $V = 12796.4(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.313$ g cm^{-3}, $2\theta_{max} = 130°$, Cu$_{K\alpha}$ ($\lambda = 1.54180$ Å), θ-2θ scan, $T = 298$ K, 3812 measured reflections, 3812 independent reflections ($R_{int} = 0.0000$) included in the refinement. Lorentzian, polarization, and ψ-scan absorption corrections were applied, $\mu = 2.998$ mm^{-1}, $[\Delta/\sigma]_{max} = 0.026$, 318 parameters refined, $R1 = 0.0540$ (for 3190 reflections with $I > 2\sigma(I)$), $wR2 = 0.1520$ (on $|F^2|$). Max./min. residual peaks in the final difference map $0.883/-0.429$ e Å^{-3}. Crystal data for **2**: Crystal dimensions 0.10 × 0.30 × 0.50 mm, monoclinic, space group $P2_1$, $a = 13.780(6)$, $b = 14.801(6)$, $c = 15.386(7)$ Å, $\beta = 114.77(1)°$, $V = 2849(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.626$ g cm^{-3}, $2\theta_{max} = 50°$, Mo$_{K\alpha}$ ($\lambda =$

0.71073 Å), θ-2θ scan, $T = 298$ K, 10115 measured reflections, 9702 independent reflections ($R_{\text{int}} = 0.0339$) included in the refinement. Lorentzian, polarization, and ψ-scan absorption corrections were applied, $\mu = 2.568\ \text{mm}^{-1}$, $[\Delta/\sigma]_{\max} = 0.046$, 734 parameters refined, $R1 = 0.0477$ (for 8333 reflections with $I > 2\sigma(I)$), $wR2 = 0.1231$ (on $|F^2|$). Max./min. residual peaks in the final difference map 0.794/ $-0.599\ \text{e}\,\text{Å}^{-3}$. Crystals of **1** and **2** were mounted in capillaries filled with drops of the mother liquor. The structures were solved by direct methods with SHELXS 86 and refined by full-matrix least-squares techniques on F^2 using SHELXL 93. For both structures, almost all non-hydrogen atoms were refined anisotropically; the MeCN solvate and two lattice H_2O molecules of **2** were refined isotropically with occupation factors fixed at 10.76 and 10.50, respectively. All hydrogen atoms in **1** were introduced at calculated positions as riding on bonded atoms. Hydrogen atoms of the methyl groups of the acetate ligands and those of C9, C23, C24, C28, C29, C30, and C31 in **2** were introduced at calculated positions as riding on bonded atoms, the remaining hydrogen atoms were located by difference map calculations and refined isotropically; no hydrogen atoms for the H_2O and MeCN solvate molecules were included in the refinement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147434 and CCDC-147435. 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).

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Core – Shell – Corona Micelles with a Responsive Shell[**]

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Supramolecular assemblies formed by self-associating block copolymers have raised considerable interest in the scientific literature.[1] In most cases, amphiphilic diblock copolymers are dissolved in a solvent selective for one constituent, which results in spherical micelles that consist of a core formed by the insoluble blocks surrounded by a shell of the solvated blocks. Although ABC triblock copolymers self-organize into a wide variety of supramolecular structures in the bulk,[1] their association in selective solvents has scarcely been studied. "Three-layer" micelles were reported in water,[2] although other micelle structures can be formed in organic solvents, as demonstrated by the so-called "Janus" micelles,[3] which consist of a cross-linked polybutadiene core and a corona with a "northern" polystyrene and "southern" poly(methyl methacrylate) hemisphere. These Janus micelles have to be distinguished from three-layer micelles, because their structure is generated in the bulk and persists in solution.

Herein we report on the formation of aqueous three-layer micelles from a polystyrene-*block*-poly(2-vinyl pyridine)-*block*-poly(ethylene oxide) triblock (PS-*b*-P2VP-*b*-PEO), these micelles will be referred to as core – shell – corona (CSC) micelles. The molecular weight of each block is 20000 for PS, 14000 for P2VP, and 26000 for PEO. CSC micelles consisting of a PS core, an intermediate P2VP layer, and a PEO corona are expected to be formed. Because the water-solubility of the central P2VP block depends on the degree of ionization,[4] the CSC micelles should be pH sensitive. Structurally they are reminiscent of the so-called "onion" micelles prepared by mixing an aqueous micellar solution of PS-*b*-P2VP diblock with P2VP-*b*-PEO chains dissolved in water.[5] At pH > 10, the P2VP blocks of the two copolymers coprecipitate, and three-layer onion micelles, that consist of a PS core, a P2VP shell, and a PEO corona are formed. The effect of pH on the onion micelles is dramatically different from that on the CSC micelles, the onion micelles disintegrate into the two constituent diblocks as the pH is decreased, which is not the case for their CSC counterparts which remain intact. Moreover, the structural features of the CSC micelles can be better controlled than those of the onion micelles.

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