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Cage Compounds

Construction of Heterometallic Cages with Tripodal Metalloligands**

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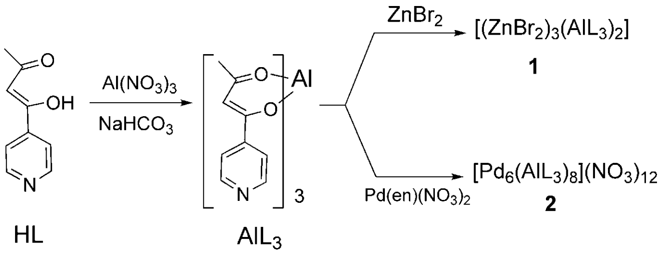
Coordination cage compounds are of great interest because of their aesthetic appeal, and properties such as guest binding and catalysis.[1] The construction of cages involves the organization of metal centers by edge-bridging or face-capping ligands.[2] Both homoleptic and heteroleptic organic ligands have been used in the preparation of cage complexes.[3] Although metalloligands have been extensively employed in the preparation of functional metal–organic frameworks,[4] fewer examples of discrete polyhedral complexes that involve the use of metalloligands have been reported.[5] Compared with organic ligands, metalloligands may function as bridging ligands with some additional advantages: 1) the introduction of new functionality, such as chirality and spectroscopic character; 2) flexible geometric control, which could avoid complex modification of the organic ligand structure; 3) the ability to assemble many components into a discrete entity.

Supramolecular chirality[6] can be generated from achiral components in coordination entities because of the asymmetric ligand arrangements.[7] One way to introduce chirality within a coordination polyhedron is the use of inherently chiral octahedral metal centers. We choose the tripodal metalloligand tris{1-(4-pyridyl)acetylacetonato}aluminum(III) (AlL_3) for the construction of chiral cages, in which the chirality arises from the trichelate Al^{III} octahedral center. The three pyridyl groups of AlL_3 can be utilized for binding additional unsaturated metal centers. Depending on the coordination preferences of the additional metal centers that are incorporated, a trigonal bipyramid $[(ZnBr_2)_3(AlL_3)_2]$ (**1**) and a capped octahedron that contains 38 components $[Pd_6(AlL_3)_8](NO_3)_{12}$ (**2**) have been isolated. In addition, the unprecedented spontaneous resolution of the chiral trigonal bipyramidal complex $[M_2M'_3L_6]$ with D_3 symmetry was observed.

The readily prepared organic ligand HL (1-(4-pyridyl)butane-1,3-dione) has a rigid molecular structure with ditopic binding sites, that is, β-diketone and pyridine units (Scheme 1). Because of the chelating nature of β-diketones and their affinity for hard metals, the neutral metalloligand AlL_3 can be readily obtained as a white powder by reacting HL with $Al(NO_3)_3$ in a 3:1 ratio under basic conditions. The ^1H NMR spectrum of AlL_3 in solution displays four singlet signals (1:1:1:1 intensity ratio), which correspond to the methyl groups, thus indicating that both *fac* and *mer* isomers are present in solution. AlL_3 is optically inactive both in the solid state or in solution, as shown by CD spectroscopy.



Scheme 1. Synthesis of the metalloligand and related complexes.

The assembly of AlL_3 and $ZnBr_2$ led to the formation of a conglomerate of homochiral crystals of $[(ZnBr_2)_3(AlL_3)_2]$ (**1**; enantiomers **1a** and **1b**). This neutral chiral molecule was synthesized by layering a solution of $ZnBr_2$ in MeOH/MeCN over a solution of AlL_3 in CH_2Cl_2. Complex **1** decomposes in DMSO, and is not soluble in solvents such as methanol and chloroform. The ^1H NMR spectrum of complex **1** showed the same patterns as the spectrum of AlL_3 in $[D_6]DMSO/CH_2Cl_2$ solution, thus indicating that **1** dissociated to AlL_3 and possible zinc complexes such as $[(DMSO)_2ZnBr_2]$. The structural determination[8] of $\mathbf{1a}\cdot 10\,H_2O$ revealed that it crystallized in the $P3_221$ space group. The molecular configuration of **1a** is a heterometallic assembly with D_3 symmetry (Figure 1 a). The five metal centers (Al_2Zn_3) are arranged in a trigonal bipyramid with an Al⋯Al separation of 11.26 Å. Each Al atom is triply chelated by the β-diketonate moieties of the ligands, and the Al–O bond lengths are in the range 1.859(4)–1.892(4) Å. Both Al^{III} centers have the Λ configuration, therefore the whole molecule is chiral. Each of the three Zn atoms is coordinated by two N donors from the pyridyl

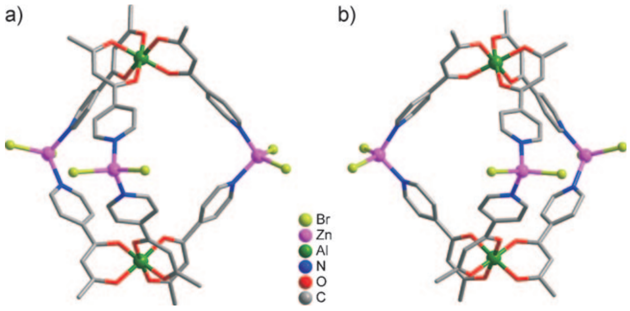


Figure 1. Chiral trigonal pyramidal $[(ZnBr_2)_3(AlL_3)_2]$ with Al atoms in a) (ΛΛ)-**1a** and b) (ΔΔ)-**1b** configurations. Hydrogen atoms are omitted for clarity.

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groups and two bromide ions with Zn–N and Zn–Br distances of 2.015(6)–2.037(6) and 2.342(1)–2.353(1) Å, respectively. The Zn atoms lie in a distorted tetrahedral environment with bond angles around the Zn^{II} centers in the range 95.6(2)–119.62(7) and 102.7(2)–111.5(2)°.

Rare examples that have a trigonal bipyramidal configuration are known.[9–11] Müller and Möller reported an interesting cluster with C_3 symmetric ligands that cover the six faces of a trigonal pyramid.[10] Although the cluster is chiral, both enantiomers are present in the same crystal ($C2/c$ space group). Raymond, Wong, and co-workers reported an elegant trigonal bipyramidal compound of type $M_2M'_3L_6$ that was prepared through a rational synthetic approach using ditopic ligands.[11] The heterometallic assembly $[Cs_4\{Ti_2(PdBr_2)_3L_6\}]$ (H_2L = 4-PPh_2-catechol) has C_{3h} symmetry, therefore it is achiral. It was proposed that the Cs^+ ion favors the formation of the achiral cluster. AlL_3 is a neutral metalloligand, so no cation effect will occur. In addition, the pyridyl group will be less likely than the phosphine moiety to generate a mirror plane in the product, as the almost-linear P–M′–P coordination was observed in the C_{3h} systems. Complex **1a** represents the first example of a chiral trigonal bipyramidal cluster that crystallizes in a chiral space group.

A single crystal of **1b** that crystallizes in the $P3_121$ space group was also structurally characterized; it was found that both Al atoms have the Δ configuration (Figure 1b). In addition, spontaneous resolution of racemic **1** into a conglomerate of homochiral crystals has been confirmed by solid-state CD spectroscopy (see the Supporting Information). The fact that only the *fac* configuration of AlL_3 is found in crystals of **1** indicates that an isomerization process (from *mer* to *fac*) occurs during the course of crystallization.

Thermogravimetric (TGA) analysis of the crystalline sample showed that **1** lost cocrystallized water molecules as the temperature was elevated. The sample decomposed when the temperature reached about 394 °C, which suggests that **1** has good thermal stability.

Further experiments revealed that different polyhedral geometries could be obtained through the use of metals with different binding preferences. The reaction of AlL_3 with $[Pd(en)(NO_3)_2]$ (en = ethylenediamine) led to the isolation of a larger cage complex $[Pd_6(AlL_3)_8](NO_3)_{12}$ (**2**), which was formed through the coordination of the pyridyl groups of AlL_3 to Pd^{II} ions (Figure 2a). The en ligand of $[Pd(en)(NO_3)_2]$ was replaced by pyridyl groups of AlL_3, in contrast to the reaction of 2,4,6-tris(4-pyridyl)-1,3,5-triazine with $[Pd(en)(NO_3)_2]$,[1a] where the en ligands were retained in the product. Treatment of AlL_3 with $Pd(NO_3)_2$ resulted in the formation of a precipitate. Structural determination showed that the cage $[Pd_6(AlL_3)_8]^{12+}$ has a capped octahedral geometry. As shown in Figure 2b–d, six Pd^{II} ions adopt an octahedral arrangement in which eight AlL_3 ligands each cap a face. The formation of complex **2** demonstrates a facile method for the organization of multiple components (38 components including 6 Pd^{II}, 8 Al^{III}, and 24 L ligands) into a large supermolecular entity through the preassembly of a metalloligand. It is noteworthy that a nanoscale hexahedron with 24 components,[2] a trigonal bipyramid with 33 units,[10] and a spherical molecule with 36 components have been reported.[12]

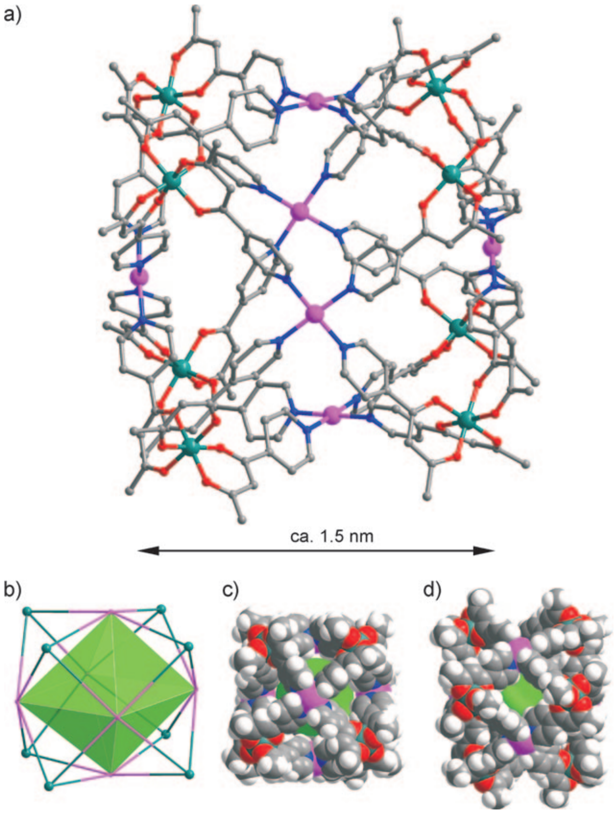

Figure 2. a) Molecular structure of the cation (ΛΛΛΛΛΛΛΛ)-$[Pd_6(AlL_3)_8]^{12+}$ in **2**, hydrogen atoms are omitted for clarity; b) the capped octahedral arrangement of Pd_6Al_8 core in $[Pd_6(AlL_3)_8](NO_3)_{12}$ (**2**); c) perspective drawing of the cation $[Pd_6(AlL_3)_8]^{12+}$ in space-filling mode; d) $[Pd_6(AlL_3)_8]^{12+}$ viewed through the Pd_2Al_2 portal. The space inside the cage is shown as a dummy green ball with diameter of ca. 10 Å. Purple Pd; cyan Al; red O; blue N; gray C; white H.

All eight Al atoms of **2** adopt the same chiral configuration, so the cation $[Pd_6(AlL_3)_8]^{12+}$ is chiral. However, the crystals are racemic because both the ΛΛΛΛΛΛΛΛ and ΔΔΔΔΔΔΔΔ enantiomers are present in the crystals of **2** with the centrosymmetric *Pcca* space group.

Complex **2** is not soluble in solvents such as methanol and chloroform. The use of DMF as a solvent gives multiple products as well as insoluble material, which hinders the study of **2** in solution.

In summary, chiral heterometallic clusters in the shapes of trigonal pyramid and capped octahedron have been prepared by using a metalloligand approach with ditopic ligands that contain β-diketone and pyridyl moieties. The spontaneous resolution of **1** has been confirmed by X-ray single crystal structure analysis and CD spectroscopy. Further work on the assembly of cage complexes by using metals of various coordination preferences is in progress.

Experimental Section

Synthesis of AlL_3: $Al(NO_3)_3 \cdot 9H_2O$ (1.19 g, 3.17 mmol) and 1-(4-pyridyl)butane-1,3-dione (1.83 g, 11.2 mmol) were dissolved in $MeOH/H_2O$ (1:1, 24 mL), then $NaHCO_3$ (1.06 g, 12.7 mmol) was added to the yellow solution; the resulting suspension was stirred for

30 min. After removal of the solvents under reduced pressure, the residue was extracted with CHCl$_3$ (2 × 45 mL), and the CHCl$_3$ solution was concentrated to a oil-like residue. Addition of EtOAc/hexane (1:1, v/v) resulted in the precipitation of a cream solid, which was dried in vacuo to give AlL$_3$ (0.755 g, 55.5 %). Elemental analysis calcd (%) for $C_{27}H_{24}N_3O_6Al$: C 63.16, H 4.71, N 8.18; found: C 62.85, H 4.68, N, 7.97; IR (KBr): $\tilde{\nu} = 1594, 1522\ \text{cm}^{-1}$ (β-diketonate).

Synthesis of **1**·10 H$_2$O: Single crystals of **1**·10H$_2$O were prepared by layering a mixed solution of ZnBr$_2$ (0.0139 g, 0.060 mmol) in MeOH/EtOH (2 mL: 2 mL) over a solution of AlL$_3$ (0.0203 g, 0.040 mmol) in CH$_2$Cl$_2$ (4 mL). Pale yellow crystals were isolated after one month (88.8 % yield). Elemental analysis calcd (%) for $C_{54}H_{48}O_{12}N_6Al_2Zn_3Br_6\cdot 2H_2O$: C 37.30, H 3.02, N 4.83; found: C 37.49, H 3.29, N 4.56; IR (KBr): $\tilde{\nu} = 1599, 1527\ \text{cm}^{-1}$ (β-diketonate).

Synthesis of **2**: To a solution of Pd(en)(NO$_3$)$_2$ (0.0185 g, 0.064 mmol) in H$_2$O/MeOH (1 mL: 2 mL) was added AlL$_3$ (0.0331 g, 0.064 mmol), and the mixture was heated to reflux for 1.5 h to give a clear solution. After filtration, the filtrate was evaporated to dryness under reduced pressure to afford a light yellow solid. The crude product was dissolved in DMF (0.5 mL), and orange crystals were deposited in ca. 25 % yield after three weeks. IR (KBr): $\tilde{\nu} = 1591, 1560\ \text{cm}^{-1}$ (β-diketonate).

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[8] Crystal data for **1a**·10H$_2$O (ΛΛ), $C_{54}H_{48}N_6O_{12}Al_2Zn_3Br_6\cdot 10\,H_2O$, $a = 13.0221(4)$, $b = 13.0221(4)$, $c = 37.656(1)$ Å, $V = 5530.0(3)$ Å^3, trigonal space group $P3_221$, $Z = 3$, $T = 173$ K, 24173 reflections measured, 9917 unique ($R_{\text{int}} = 0.1205$), final $R1 = 0.0498$, $wR2 = 0.0776$ for 3437 observed reflections [$I > 2\sigma(I)$]; Flack parameter = 0.02(1). Crystal data for **1b**·3 H$_2$O (ΔΔ), $C_{54}H_{48}N_6O_{12}Al_2Zn_3Br_6\cdot 3\,H_2O$, $a = 12.977(1)$, $b = 12.977(1)$, $c = 37.903(3)$ Å, $V = 5527.9(8)$ Å^3, trigonal space group $P3_121$, $Z = 3$, $T = 173$ K, 18978 reflections measured, 8710 unique ($R_{\text{int}} = 0.0964$), final $R1 = 0.0625$, $wR2 = 0.1352$ for 4309 observed reflections [$I > 2\sigma(I)$]; Flack parameter = −0.005(15). Crystal data for **2**, $C_{216}H_{192}N_{36}O_{84}Al_8Pd_6$, $a = 30.0273(6)$, $b = 31.0679(5)$, $c = 38.8047(3)$ Å, $V = 36200(1)$ Å^3, orthorhombic space group *Pcca*, $Z = 4$, $T = 126$ K, 87117 reflections measured, 27421 unique ($R_{\text{int}} = 0.0568$), final $R1 = 0.0663$, $wR2 = 0.1670$ for 9609 observed reflections [$I > 2\sigma(I)$]. CCDC 737668 (**1a**), 737669 (**1b**) and 737670 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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