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Synthesis and structure of a novel supramolecular Zn_3Co_8 assembly containing a linear Zn_3 core†

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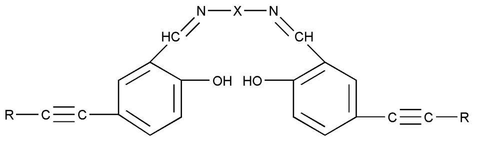
Reaction of $Zn(OAc)_2·2H_2O$ (OAc = acetate) with LH_2 in THF followed by reaction with $Co_2(CO)_8$ yields the novel supramolecular assembly $Zn_3L_2(OAc)_2[Co_2(CO)_6]_4·0.5CH_2Cl_2$, which was characterized by X-ray diffraction (LH_2 = $(CH_2)_3(N{=}CH\text{-}2\text{-}OH\text{-}5\text{-}C{\equiv}CSiMe_3C_6H_3)_2$ or *N*,*N′*-propylenebis(2-hydroxy-5-trimethylsilylethynl-1-aldimine).

New supramolecular assemblies of metals are currently of interest for their potential uses in a large variety of different applications. These range from electronic, photonic and mechanical devices of importance to nanotechnology[1] to the control of redox activity, magnetic and luminescence properties as well as anion recognition and electrochemical sensing.[2]

As part of a broad study involving the use of multidentate ligands for the building blocks of new supramolecular assemblies we recently investigated the use of new Schiff base ligands[3] of type **A** with a variety of metal complexes (Scheme 1). These ligands have been specifically designed with functional acetylenic groups (–C≡C–R) in order to provide sites for additional reactivity and/or binding or complexation. We report here the synthesis and structure of a novel trinuclear zinc(II) derivative **1** in which the acetylenic groups are involved in binding to dicobalt units. The resulting assembly contains eight Co and three Zn atoms.

Although complexes involving three zinc atoms are known,[4,5] the linear Zn_3 arrangment appears to be rare.[5] The zinc(II) ion plays an important role in many biological systems such as metalloenzymes[6] and in most cases where structural studies are available it has been found to have a distorted four- or five-coordinate stereochemistry.[7] A number of model complexes of zinc have been prepared in order to improve our understanding of the structure–reactivity relationship of the active site(s) of such metalloenzynes.[6–8] Many of these studies involve the use of multidentate N and O donors including those based on Schiff-base and related ligands.[9] There are relatively few well characterized tetradentate Schiff-base complexes of Zn(II). The first structurally characterized complex salen·ZnH_2O has an unusual supramolecular structure formed by strong hydrogen bonding of the coordinated water molecule.[10] This produces an infinite one-dimensional polymer which is no doubt the reason for the very low solubility of the complex in common organic solvents. Singer and Atwood addressed the solubility issue by the use of *tert*-butyl substituted ligands and were able to isolate and characterize a number of new salen(^{t}Bu) complexes of zinc.[11]

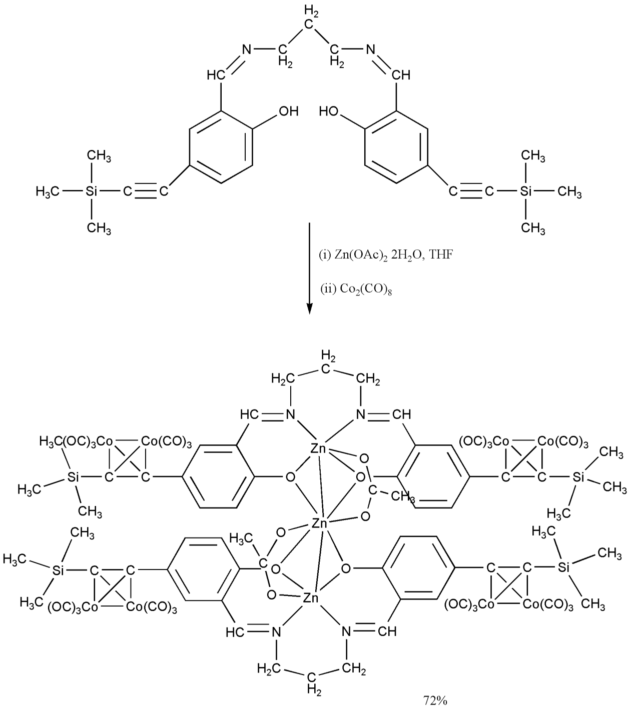
In our hands reaction of the ligand **A** (X = $(CH_2)_3$, R = $SiMe_3$, Scheme 1) with $Zn(OAc)_2·2H_2O$ in THF at room temperature gave an insoluble green material. However, subsequent treatment of this solid with a solution of $Co_2(CO)_8$ in THF gave a dark green solution from which dark green crystals of the novel supramolecular assembly **1** were isolated in 72% yield (Scheme 2).‡ The compound is only sparingly soluble in organic solvents and decomposes in solution to give unidentified products. Since we were unable to obtain reliable NMR data in solution, structural information in the solid state was provided by an X-ray crystallographic study.



A

X = spacer unit,
R = alkyl, aryl,etc

Scheme 1



Scheme 2

Molecules of **1** crystallize in the triclinic space group $P\bar{1}$ with one molecule per unit cell (Fig. 1). The overall molecular framework contains a central linear Zn_3 core in which the terminal Zn atoms are coordinated in a distorted square planar fashion by the N_2O_2 atoms of the ligand.[12] The central zinc atom (Zn(2)) lies on a crystallographic inversion center at ½, ½, ½, and is bonded to two acetate units which bridge to the terminal zincs. This arrangement gives each terminal zinc atom a five-coordinate square-based pyramidal geometry while the central zinc atom has pseudo-octahedral coordination. The Zn–O and Zn–N bond lengths for **1** are unexceptional while the Zn–Zn distance of 3.064(2) Å is fairly short for a non-bonded distance bridged by acetate and alkoxide groups.[9,13] However, it is still longer than the sum of the van der Waals radii for two Zn(II) atoms (2.8 Å).[14]

On the periphery of the assembly each acetylinic unit is bonded to a $Co_2(CO)_6$ group. The bonding in each Co_2C_2 unit is typical of that which is commonly formed when $Co_2(Co)_8$ reacts with acetylenes.[15] The $Co_2(CO)_6C_2SiMe_3$ groups have con-

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† Electronic supplementary information (ESI) available: X-ray experimental and data. See http://www.rsc.org/suppdata/cc/b2/b209785k/

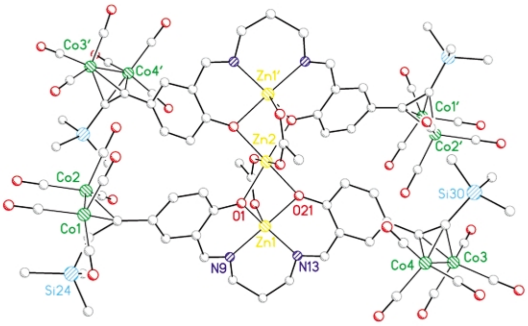

Fig. 1 View of **2** with hydrogen atoms omitted for clarity. Color code: zinc: orange; cobalt: green; silicon: pale blue; oxygen: red; nitrogen: blue: Zn(1)–Zn(2) 3.064(2), Zn(1)–O(1) 1.981(9), Zn(1)–O(34) 2.001(10), Zn(1)–N(13) 2.003(11) Å

siderable steric bulk and it seems likely that in order to minimize repulsions between these outlying groups the two Schiff base ligands (L) adopt a configuration which maximizes their distances apart. In addition in binding to the zinc, each ligand has a distinctly curved structure. This shallow dish or bowl-like architecture also helps to minimize steric interactions between pairs of Co_2 units. Fig. 2 illustrates this aspect of the structure with a view along the Zn_3 axis.

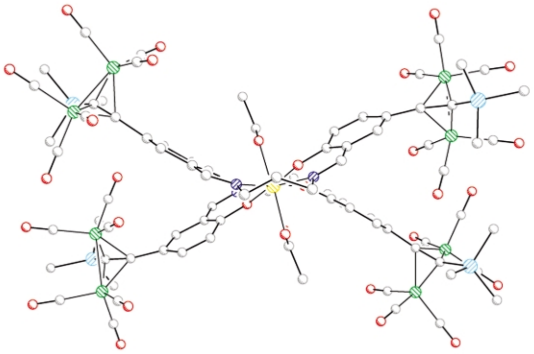

Fig. 2 View down the Zn_3 axis showing the curvature and relative orientation of each ligand.

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Notes and references

‡ *Preparation* of $Zn_3L_2(OAc)_2[Co_2(Co)_6]_4{\cdot}0.5CH_2Cl_2$: L = $(CH_2)_3(N{=}CH\text{-}2\text{-}O\text{-}5\text{-}C{\equiv}SiMe_3C_6H_3)_2$. The free ligand LH_2 was prepared as a yellow solid from 1,3-diaminopropane and 5-bromosalicyaldehyde in ethanol followed by reaction with $Me_3SiC{\equiv}CH$, $Pd(Ph_3P)_4$, CuI and diisopropylamine in benzene using well established procedures. A solution of LH_2 (0.38 g, 0.8 mmol) in THF was added to $Zn(OAc)_2{\cdot}2H_2O$ (0.26 g, 1.2 mmol). The mixture was stirred (12 h) at room temperature during which time a green suspension formed. Volatile materials were removed in *vacuo* and the residue was washed with *n*-pentane (2 × 15 mL). A solution of $Co_2(CO)_8$ (0.54 g, 1.6 mmol) in THF (40 mL) was then added giving a dark green solution. After 4 h the solution was filtered, and volatile materials removed in *vacuo*. The dark green residue was extracted with dichloromethane, the solution filtered, and methanol was added to the filtrate to give dark green crystals of **1**. They were collected and dried in *vacuo*. Yield 0.7 g, 72%, mp > 260 °C. MS (Finnigan Mat. TSQ700; FAB/triethanolamine): m/z = 907.9 $(M - (C_2Co_2SiMe_3)_4)^+$.

Crystal data for **1**:$C_{83}H_{68}Cl_2Co_8N_4O_{32}Si_4Zn_3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.5797(7)$, $b = 14.5872(10)$, $c = 21.596(2)$ Å, $\alpha = 75.866(2)$, $\beta = 85.668(2)$, $\gamma = 80.523(5)°$, $V = 2583.5(4)$ Å^3, $Z = 1$, $D_c = 1.597$ g cm^{-3}, $\mu = 2.105$ cm^{-1}, $\lambda = 0.71073$ Å, $T = 153$ K, $F(000) = 1246$, for 6742 independent reflections, $R_1 = 0.0964$ $[I > 2\sigma(I)]$, $wR_2 = 0.1658$, GOF on $F^2 = 1.133$, diff. peak/hole (e Å^{-3}) = 0.715/−0.591. Data were collected on a Nonius Kappa CCD diffractometer and the structure solved using the program SHELXL-97. CCDC 195105. See http://www.rsc.org/suppdata/cc/b2/b209785k/ for crystallographic data in CIF or other electronic format.

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