Synthesis and structure of the hexameric, dodecanuclear metallamacrocycle [(5-methyl-3-phenylpyrazole)$_2$Zn$_2$(OCH$_2$CH$_2$S)]$_6$†

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A metallamacrocycle containing twelve Zn^{2+} ions, making it the largest member of a family of pyrazole-bridged cyclic metal clusters, has been synthesized and structurally characterized from the reaction of [Zn(ClO$_4$)$_2$] with 5-methyl-3-phenylpyrazole, 2-mercaptoethanol, and NaOH.

Metal-containing macrocyclic structures are an active area of research in the field of supramolecular coordination chemistry.[1] Many examples of such structures have appeared in the literature, using a variety of metals and ligands.[2] Metallamacrocycles formed from pyrazole anions that act as bridging ligands[3] have been reported containing from three to as many as eight metal centers connected by an equal number of pyrazolate ligands. Some of these metallamacrocycles have found utility in the synthesis of self-assembled supramolecular metallomesogens.[4] Among this pyrazole family of metallamacrocycles, the highest nuclearity structure reported to date is of [Cu$_8$(dmpz)$_8$(OH)$_8$] (dmpz = 3,5-dimethylpyrazole), which contains eight Cu^{2+} centers.[5] Herein we report the first example of a dodecanuclear pyrazolate metallamacrocycle that contains 2-mercaptoethanol as a second bridging ligand.

The macrocyclic complex was initially isolated from the thermal decomposition of the mononuclear metal complex [(Tp^{Ph,Me})ZnOH] in the presence of 2-mercaptoethanol.[6,7] Subsequently, a reliable, direct synthesis of [(5-methyl-3-phenylpyrazole)$_2$Zn$_2$(OCH$_2$CH$_2$S)]$_6$ (**1**) was achieved by first combining zinc perchlorate with 5-methyl-3-phenylpyrazole and NaOH in hot MeOH, followed by addition of 2-mercaptoethanol (Scheme 1).‡ This procedure gave **1** upon recrystallization in ~20% yield as small, colorless blocks.

The X-ray structure of **1**§ revealed a molecular ring composed of twelve zinc atoms, twelve molecules of 5-methyl-3-phenylpyrazole, and six 2-mercaptoethanol molecules (Fig. 1). The rings are discrete and neutral as the +24 charge of the twelve Zn^{2+} centers is balanced by the twelve deprotonated pyrazole rings and the six doubly deprotonated 2-mercaptoethanol molecules. Each 2-mercaptoethanol unit connects a total of three Zn^{2+} centers together, with both the oxygen and sulfur atoms acting as bridging η^2-donors. The 2-mercaptoethanol ligands are located on the inside of the ring and the connectivity is such that two distinct zinc centers are formed. Each Zn^{2+} sits in a distorted tetrahedral coordination environment with two nitrogen donors (from two different pyrazole ligands, av. Zn–N 1.984 Å), one oxygen donor (av. Zn–O 1.979 Å), and one sulfur donor atom (av. Zn–S 2.328 Å). However, one set of zinc centers is bound by the oxygen and sulfur atoms of the same 2-mercaptoethanol molecule, while the second set of zinc ions is bound by the oxygen and sulfur atoms of two separate 2-mercaptoethanol molecules (Fig. S1†). Each pyrazole ring bridges two zinc centers, but there are two distinct types of pyrazole ligands in the structure. One set of pyrazole ligands bridges two zinc ions that have an η^2-oxygen bound between them from a 2-mercaptoethanol molecule. These pyrazole ligands decorate the outer edge of the ring, with the phenyl substituents situated tangentially to the circumference of the ring. The second set of pyrazole ligands lies on the upper and lower rims of the ring, and bridges two zinc ions that share a sulfur donor atom. The Zn–Zn distance in the cluster is 3.27 Å.

Despite the apparent propeller twist seen in Fig. 1, the central pore of the ring sits on the crystallographic −3 axis and therefore the chirality of the metal centers alternates around the ring (Fig. S2†) generating an overall achiral structure. The ring is a sizable complex with an outer diameter of just over 23 Å, a height of ~10.9 Å, and an inner pore diameter of ~4.7 Å.[8] Surprisingly, no solvent molecules were found in the solid-state structure. No time was allowed for solvent evaporation from the crystals, as they were quickly transferred from the mother liquor to Paratone oil and then rapidly flash frozen in a stream of cold air (−173 °C). However, upon standing in Paratone oil at
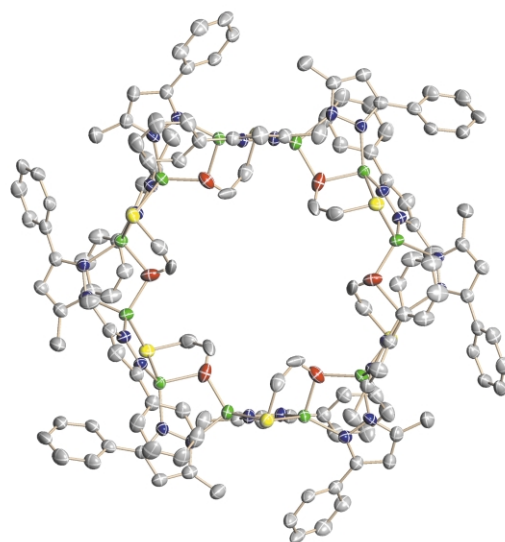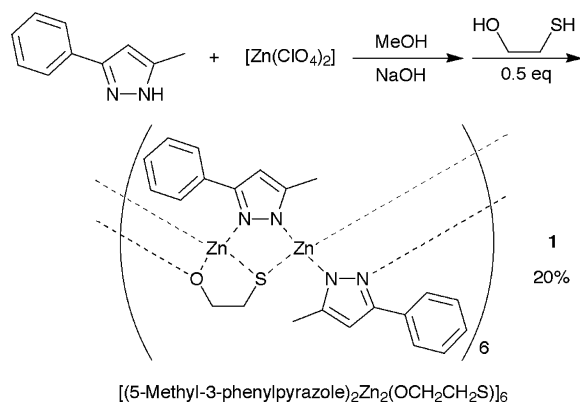
[(5-Methyl-3-phenylpyrazole)$_2$Zn$_2$(OCH$_2$CH$_2$S)]$_6$

Scheme 1

† Electronic supplementary information (ESI) available: crystal structure diagrams. See http://www.rsc.org/suppdata/cc/b3/b300453h/

Fig. 1 Diagram of the molecular hexagon **1** (ORTEP, 50% probability ellipsoids). Carbon (gray), nitrogen (blue), oxygen (red), sulfur (yellow), and zinc (green) atoms shown; hydrogen atoms are omitted for clarity.

ambient temperature the crystals cracked and typically became opaque, indicating a loss of crystal integrity. Elemental analysis of dried crystals was consistent with the solventless metal-lamacrocycle.‡ TGA experiments were also performed to evaluate the solvent content of the crystals. Crystals dried *in vacuo* overnight or in air for ~30 min produced an average weight loss of 2.75% when heated from room temperature to 150 °C. Cooling of these crystals, followed by a second TGA experiment on the same sample yielded an average loss of 0.67%. Storage of the sample in air overnight, followed by TGA analysis, gave a weight loss of 1.30%. Based on these data, the small weight loss observed from the crystals is attributed to absorbed moisture from the atmosphere. These observations, combined with the handling of the crystals prior to data collection, suggest that the crystal may contain extremely disordered, weakly associated solvent molecules that could not be found during the structure determination and are easily liberated upon exposure to air.

A notable feature about the solid-state structure of **1** is the arrangement of the molecules in the crystal lattice. The rings are perfectly aligned along the crystallographic *c*-axis, making uninterrupted channels through the solid (Fig. 2). As mentioned above, no solvent molecules were found occupying the channels and because the complex is neutral there are no counterions to occupy the available void space. The channels in the solid-state structure of **1** are similar to those found in the octameric complex $[Cu_8(dmpz)_8(OH)_8]$, which were appropriately described as "zeolite-like."[5] $[Cu_8(dmpz)_8(OH)_8]$ was found only to crystallize as a clathrate with nitrobenzene and possessed additional unresolved electron density within the pores that were proposed to be water or some other disordered solvent.[5] In the structure of **1** no cocrystallized solvent could be resolved, although the physical behaviour of the crystals suggests the presence of some weakly confined solvent (*vide supra*).

The synthesis of a large metallamacrocycle **1** has been achieved from both the thermal rearrangement of a mono-nuclear zinc complex and directly from zinc perchlorate, 5-methyl-3-phenylpyrazole, NaOH, and 2-mercaptoethanol. This complex represents the largest such cluster based on bridging pyrazole ligands. The macrocycles are arranged in the solid state such that channels with a diameter of ~4.7 Å are formed throughout the crystalline lattice. Efforts are currently under way to further explore other members of this cluster motif and to examine their host–guest chemistry.
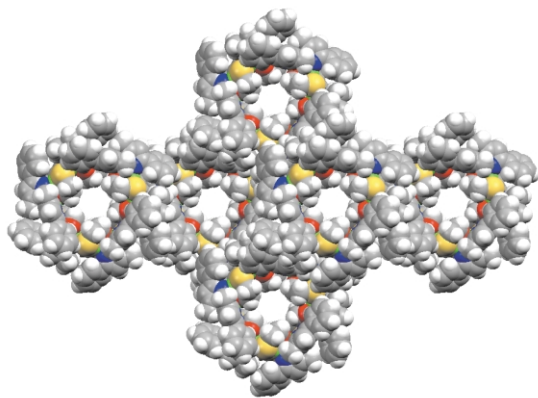
Fig. 2 Spacefilling packing diagram of the crystal lattice **1** viewed along the crystallographic *c*-axis. Carbon (gray), hydrogen (white), nitrogen (blue), oxygen (red), sulfur (yellow), and zinc (green) atoms shown.

Notes and references

‡ Synthesis of **1**. Reactions were preformed under an atmosphere of nitrogen. *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.* 5-Methyl-3-phenylpyrazole (0.425 g, 2.7 mmol) and NaOH (0.108 g, 2.7 mmol) were heated to reflux in 50 mL of MeOH, until both components dissolved. Upon dissolution, $[Zn(ClO_4)_2]$ (1.0 g, 2.7 mmol) in 80 mL of MeOH was added to the solution. The mixture was heated to reflux for 2.5 h, after which 2-mercaptoethanol (94 μL, 1.3 mmol) in 25 mL of MeOH was added to the solution. The mixture was heated to reflux for 3 h and then evaporated to dryness to obtain an off-white solid. The product was recrystallized from a ~2 : 5 mixture of MeOH : benzene diffused with pentane over a period of ~1 week, resulting in colorless crystals of **1** in 20% yield. The crystals decomposed upon heating in the range of 280–285 °C. Anal. Calcd for $C_{132}H_{132}N_{24}O_6S_6Zn_{12}$: C, 50.69; H, 4.25; N, 10.75 Found C, 50.98; H, 4.45; N, 11.01.

§ Crystal data for **1**, $C_{132}H_{132}N_{24}O_6S_6Zn_{12}$: M_r = 3127.42, rhombohedral, $a = b$ = 29.6563(18) Å, c = 19.187(3) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 14614(2) Å^3, T = 100(2) K, space group $R\bar{3}$, Z = 3, μ(Mo-K$_\alpha$) = 1.556 mm^{-1}, 24253 reflections measured, 5294 (R_{int} = 0.0518), d_{calc} = 1.280 g cm^{-3}, R_1 = 0.0634, wR_2 = 0.1949 (for $I > 2\sigma$). Data was collected on a Brucker AXS area detector diffractometer. The crystal was mounted on a quartz capillary by using Paratone oil and was cooled in a nitrogen stream on the diffractometer. The structure was solved and refined as described in ref. 7. All hydrogen atoms were fixed at calculated positions with isotropic thermal parameters; all non-hydrogen atoms were refined anisotropically. See http://www.rsc.org/suppdata/cc/b3/b300453h/ for crystallographic data in .cif or other electronic format. CCDC reference number 188512.

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