



SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW RHOMBOID $\{Mn^{II}_2Mn^{III}_2\}$ CLUSTER BASED ON CALIX[4]ARENE AND BATHOPHENANTHROLINE LIGANDS

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A. S. Ovsyannikov,^{*a} I. V. Strelnikova,^{a,b} A. A. Iova,^b D. R. Islamov,^c
P. V. Dorovatovskii,^d S. E. Solovieva,^b and I. S. Antipin^b

^a Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center,
Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Russia

^b Kazan Federal University, ul. Kremlevskaya 18, Kazan, 420008 Russia

^c Laboratory for Structural Analysis of Biomacromolecules, FRC Kazan Scientific
Center, Russian Academy of Sciences, ul. Lobachevskogo 2/3, Kazan, 420111 Russia

^d National Research Centre "Kurchatov Institute",
pl. Akademika Kurchatova 1, Moscow, 123182 Russia

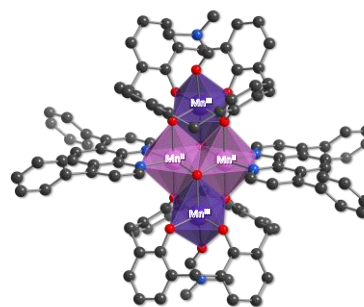
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Abstract

A cooperative coordination of calix[4]arene and bathophenanthroline, acting as a bidentate N,N-donor coligand, with manganese(II) ions led to the formation of a new tetranuclear $\{Mn^{II}_2Mn^{III}_2\}$ cluster in the crystalline phase. The X-ray diffraction analysis revealed the generation of a symmetrical metal cluster core, displaying a rhomboid geometry around Mn ions, resulting in extremely short distances between the metal ions compared to the previously reported calix[4]arene-supported mixed-valence tetranuclear manganese clusters.



Key words: calix[4]arene, bathophenanthroline, Mn(II), Mn(III), cluster.

Introduction

Single molecule magnets (SMMs) have attracted a growing interest owing to their fascinating ability to exhibit slow magnetic relaxation behavior during long time in the absence of an external magnetic field, which can find application in the development of quantum spintronics for data storage or operating [1–9]. Calix[4]arenes, which are composed of four phenolic units connected *via* CH₂ bridges (Fig. 1), represent an especially suitable molecular platform for the design of SMMs [10, 11]. When combined with Mn^{II/III} ions both with or without 4*f* metal ions, calix[4]arenes **1–4** are prone to form metal clusters, which nuclearity, self-assembly in the crystalline phase, and magnetic properties (including SMM behavior) can be controlled *via* either an upper rim or functionalization of CH₂ bridges, or the nature of the used coligands [12–20]. Among them, $\{Mn^{II}_2Mn^{III}_2\}$ systems are of particular interest because their magnetic properties can be finely tuned by varying the nature of the monodentate or bidentate (chelating) coligands coordinated to Mn(II) atoms located at the side position of the cluster core [21–23]. Recently, the formation and magnetic properties of a series of clusters, containing a $\{Mn^{II}_2Mn^{III}_2\}$ metal core, generated by the co-ordination of calix[4]arenes **2** or **3** with N,N-donor ligands such as 2,2'-bipyridine [21] and 1,10-phenanthroline [12] have been reported. It was demonstrated that the magnetic properties of these fascinating coordination compounds are strongly related to the distances between Mn^{II/III} ions within the rhomboid metal core, which distortion magnitude can be tuned by varying N,N-donor coligands.

Herein, we report on the synthesis and crystal structure of a

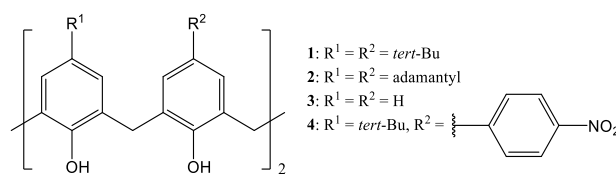


Figure 1. Calix[4]arenes involved in the formation of Mn^{II}/Mn^{III} mixed-valence polynuclear clusters.

new $\{Mn^{II}_2Mn^{III}_2\}$ cluster supported by calix[4]arene **3** (R = H, Fig. 1) and bathophenanthroline (**bathophen**), acting as an N,N-donor auxiliary ligand, which leads to unprecedentedly short distances between the metal ions within the cluster core.

Results and discussion

The coordination of ligand **3** with MnCl₂ in presence of **bathophen** and NEt₃ in a 3/MnCl₂/**bathophen**/NEt₃ ratio of 1/4/4/10 in DMF/MeOH in the air resulted in the formation of violet complex monocrystals after slow evaporation. According to the results of single-crystal X-ray diffraction analysis, the complex of formula [C₁₁₀H₈₆N₆O₁₂Mn₄]·2(MeOH) (**3**₂-**Mn**₄(**bathophen**)₂) (Fig. 2, Table S1 in the Electronic supplementary information (ESI)) represents a centrosymmetric sandwich-like structure, where a Mn₄-rhomboid core is held between two calix[4]arene ligands, adopting a slightly deformed *cone conformation* of the macrocyclic backbone (dihedral angle between the opposite aryl units are 70.1(1)° and 77.3(1)°), and two **bathophen** ligands. Mn(2) atoms form the coordination bonds with four O atoms, belonging to the deprotonated phenolate units of calix[4]arene **3**, with Mn(2)...O distances

equal to 1.894(2) Å, 1.915(2) Å, 1.936(2) Å, 1.954(2) Å, one O atom of a DMF molecule and one O atom, coming from a μ_3 -OH bridging moiety ($d_{\text{Mn}(2)\dots\text{O}} = 2.290(2)$ Å and 2.255(2) Å, respectively). In contrast to Mn(2) atoms, Mn(1) atoms are located at the side positions of the cluster core, coordinating one **bathophen** molecule ($d_{\text{Mn}(1)\dots\text{N}} = 2.059(2)$ Å and 2.055(2) Å), two calix[4]arene molecules ($d_{\text{Mn}(1)\dots\text{O}} = 2.196(2)$ Å and 2.179(2) Å), as well as two μ_3 -OH bridges ($d_{\text{Mn}(1)\dots\text{O}} = 1.869(2)$ Å and 1.872(2) Å). It is worth noting that the observed Mn(1)...N coordination bond lengths appeared to be significantly lower than those in the previously reported analogs: 2.220(7)–2.259(8) Å [20], 2.175(3) Å, and 2.272(3) Å [12] for 2,2'-bipyridine-containing complexes and 2.21(1)–2.237(7) Å for phenanthroline-based compound [12]. The coordination bond angles for **3**₂-Mn₄(bathophen)₂ are listed in Table S2 in the ESI.

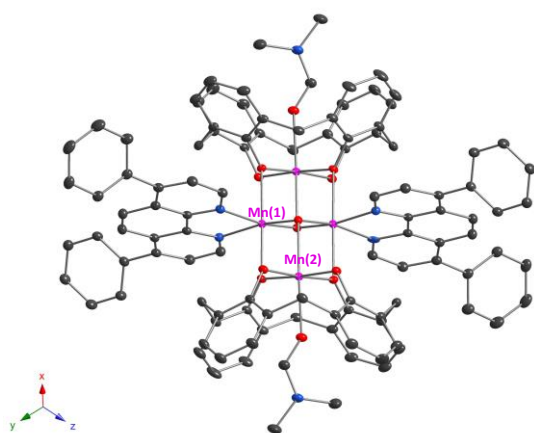


Figure 2. ORTEP view of **3**₂-Mn₄(bathophen)₂ with 30% probability of thermal ellipsoids. C, O, N, and Mn are represented by dark-grey, red, blue, and rose ellipsoids, respectively. The hydrogen atoms and solvate molecules are omitted for clarity.

According to the *SHAPE* analysis [24], both Mn atoms display a slightly distorted octahedral geometry (Table S3 in the ESI). A comparison of the observed coordination bonds with the literature data [12, 21–23] allows for assuming that Mn(1) and Mn(2) atoms are in +3 and +2 oxidation states, respectively.

As a result, the involvement of bathophenanthroline in the coordination with a {Mn₄} cluster leads to a decrease in Mn(II)...Mn(II) distance up to 2.6654(8) Å, which magnitude significantly exceeds this one observed for all earlier reported calix[4]arene-supported {Mn₄} clusters [12, 20–23]. Moreover, Mn(II)...Mn(III) distance is also found to be decreased (3.163(1) Å and 3.180(1) Å) compared to this one evidenced for the **3**-based {Mn₄} cluster containing 2,2'-bipyridine (3.224(2)–3.360(2) Å) [20].

In terms of crystal packing, the cluster species are stacked into parallel 2D layers along *y*0*z* plane due to the weak intermolecular CH/π interactions, involving C atoms from the aryl calix[4]arene units and the aromatic system belonging to phenyl substituents of bathophenanthroline moieties ($d_{\text{C31}\dots\text{C6centroid}} = 3.638(2)$ Å, $d_{\text{C34}\dots\text{C6centroid}} = 3.696(2)$ Å, Fig. 3). As a result, the shortest {Mn₄}...{Mn₄} distances of 11.700(2) Å, 15.170(2) Å, 15.380(2) Å are observed in crystal. Each of two solvate MeOH molecules is found to be H-bonded with O

atom of the phenolate unit, belonging to the calix[4]arene platform ($d_{\text{O}(7)\dots\text{O}(5)} = 2.784(2)$ Å, Fig. S1 in the ESI).

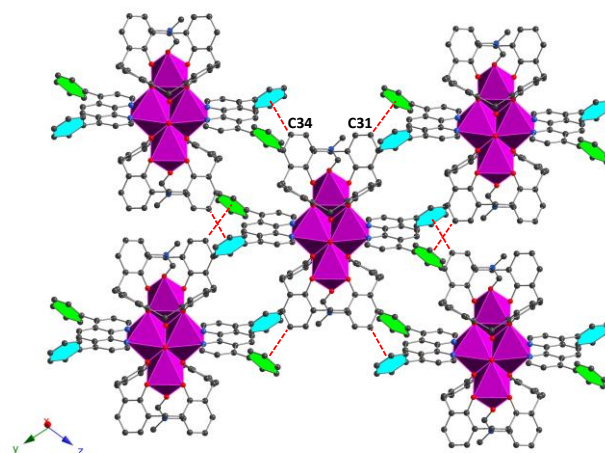


Figure 3. Fragment of the crystal packing of **3**₂-Mn₄(bathophen)₂ showing the formation of a 2D layer supported by weak CH/π interactions (denoted as red dashed lines) between the cluster species and orientated along *y*0*z* plane. The hydrogen atoms and solvate molecules are omitted for clarity.

Experimental section

General remarks

All chemicals were purchased from commercial sources and used without additional purification. The solvents were purified according to the standard protocols. Calix[4]arene **3** was synthesized using the earlier reported method [25]. The elemental analyses were performed on a EuroEA 3028-HT-OM Eurovector S.p.A. unit (Italy).

Crystallization conditions

[Mn^{II}₂Mn^{III}₂(μ_3 -OH)₂(**3**)₂(bathophen)₂·2(CH₄O)] (**3**₂-Mn₄(bathophen)₂). Calix[4]arene **3** (25 mg, 0.059 mmol), MnCl₂·4H₂O (45.5 mg, 0.236 mmol), and bathophenanthroline (78.3 mg, 0.236 mmol) were mixed in a DMF/MeOH solution (*v/v* = 1/1, 20 mL) in the air followed by the addition of triethylamine (0.070 mL, 0.590 mmol), affording a dark-violet solution. The reaction mixture was stirred at room temperature for 1 h and then filtered. The slow evaporation of the filtrate afforded single crystals suitable for X-ray diffraction analysis in 3 days. Yield: 29 mg, 50%. Anal. Calcd. for C₁₁₂H₉₄Mn₄N₆O₁₄: C, 68.36; H, 4.82; N, 4.27. Found: C, 68.49; H, 4.85; N, 4.32%.

Conclusions

The new {Mn^{II}₂Mn^{III}₂} tetranuclear cluster supported by both calix[4]arene and bathophenanthroline ligands was prepared and structurally characterized using single-crystal X-ray diffraction analysis. It was revealed that the involvement of bathophenanthroline in coordination with Mn(II) atoms led to the realization of unprecedentedly short Mn(II)...Mn(II) and Mn(II)...Mn(III) distances within the cluster core. Notably, the shortening of intermetal distances was accompanied by significant enhancement of the coordination bonding between Mn(II) and N atoms of the N,N-donor coligand, demonstrating

exceptionally unusual coordination behavior compared to the reported analog. The magnetic properties study of the resulting coordination compound is currently under investigation in order to establish the impact of the structural transformations of the calix[4]arene-supported $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2\}$ cluster, evolved by the coordination with the bathophenanthroline coligand.

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Corresponding author

* E-mail: osaalex2007@rambler.ru. Tel: +7(965)604-5306 (A. S. Ovsyannikov).

Electronic supplementary information

Electronic supplementary information (ESI) available online: [the detailed crystallographic and SHAPE analysis data](#). For ESI, see DOI: 10.32931/ioXXXXx.

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