Journal of Molecular Structure 1081 (2015) 217–223

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Experimental and theoretical study of the influence of peripheral environment on magnetic properties of tetranuclear manganese skeleton in new representatives of calix[4]arene-containing [Mn^{II}_2 Mn^{III}_2] clusters

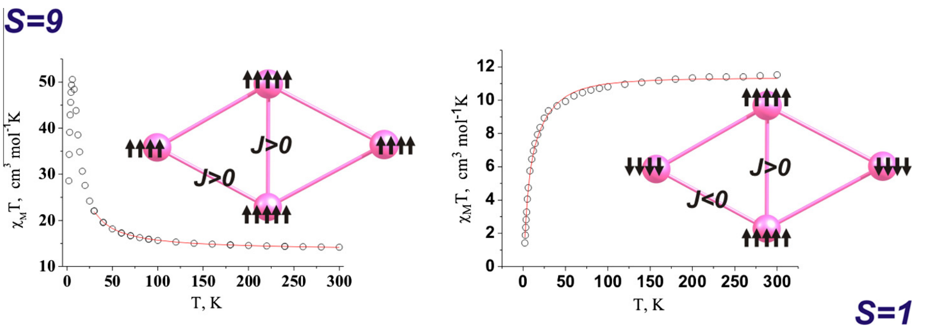
S.M. Aldoshin [a], I.S. Antipin [b], S.E. Solov'eva [b], N.A. Sanina [a], D.V. Korchagin [a], G.V. Shilov [a], F.B. Mushenok [a], A.N. Utenyshev [a], K.V. Bozhenko [a,*]

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1, Acad. Semenov av., Chernogolovka 142432, Moscow Region, Russia
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center Russian Academy of Sciences, 8, Arbuzov str., Kazan 420088, Tatarstan Republic, Russia

HIGHLIGHTS

- A new representative of calix[4]arene-containing Mn4-core complex with 2,2′-dipyridyl ligand was synthesized.
- The crystal structure and magnetic properties of this complex have been studied.
- The control of the exchange coupling interaction type can be provided by peripheral ligands.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 10 October 2014
Accepted 10 October 2014
Available online 17 October 2014

Keywords:
Polynuclear complexes of manganese
Molecular magnets
Calix[4]arenes
X-ray analysis
SQUID magnetometry
Quantum-chemical calculations

ABSTRACT

A new representative of calix[4]arene-containing tetranuclear manganese complexes of [$Mn_2^{III}Mn_2^{II}$] type with 2,2′-dipyridyl bidentate ligand coordinated in the equatorial plane of the complex (**II**) has been obtained. The complex is crystallized in monoclinic space group $P2_1/c$ ($a = 14.9402(7)$ Å, $b = 32.816(1)$ Å, $c = 21.595(1)$ Å, $\beta = 106.888(4)$). Its magnetic properties have been studied by the method of SQUID magnetometry. The substitution of a peripheral ligand was shown to influence substantially on the structure of the central fragment of the metal complex, and, hence, on the magnetic properties. Quantum-chemical calculations were performed for this complex and for the similar calix[4]arene-containing manganese complex with pyridine ligand (**I**). The influence of peripheral environment on the magnetic properties of tetranuclear manganese skeleton was elucidated for both complexes.

Introduction

As mentioned previously [1], after the discovery of molecular magnetism (Single-Molecular Magnetism, SMM) in complex $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$, known as Mn_{12} [2,3], the interest to polynuclear metal complexes, in particular, to manganese complexes, increased. However, in spite of serious investigations in this field [4,5], only ten and a half years later a monomolecular magnet based on hexanuclear manganese complex (Mn_6) was obtained [6]. Unfortunately, there are no clear recommendations on the synthesis of monomolecular magnets with pre-set properties. For example, the intention to increase substantially the total spin of the complex led to the synthesis of manganese cluster Mn_{19} with

---

[*] Corresponding author. Tel.: +7 496 522 12 61; fax: +7 496 522 35 07.
E-mail address: bogenko@icp.ac.ru (K.V. Bozhenko).

http://dx.doi.org/10.1016/j.molstruc.2014.10.022

spin $S = 83/2$, which, however, did not possess the properties of bistability [7]. The Brechin's group, which earlier synthesized complex Mn_6 with the improved characteristics, recently [8] obtained and characterized a family of calix[4]arene-containing mixed valence tetranuclear manganese complexes, exhibiting properties of molecular magnet at a temperature $\leqslant 1.1$ K. Calixarenes are available polydentate ligands with the structural potential for their modification (variation of substituents, bridging fragments between the phenyl rings, and amount of structural units in the calixarene molecule) [9–11]. In addition, calixarene-containing $[Mn^{II}_2Mn^{III}_2]$ clusters can be modified by the variation of the monodentate external ligands. In [1] we reported the synthesis, structure and properties of a new representative of calix[4]arene-containing tetranuclear manganese complexes of $[Mn^{II}_2Mn^{III}_2]$ type (**I**) with pyridine ligand coordinated in the equatorial plane of the complex. This complex has properties of a monomolecular magnet at temperatures below 5 K. Its exchange coupling parameters were determined experimentally: $J_{wb} = 1.49$ K ($1.0\ cm^{-1}$), $J_{bb} = 3.84$ K ($2.56\ cm^{-1}$) and activation energy $\Delta E = 29.4$ K. As follows from quantum-chemical calculations of the electronic structure of complex **I** performed by the DFT method at the B3LYP/LANL2DZ level of theory using the GAUSSIAN-03 program [12] with the fixed geometry obtained by X-ray crystallography, the ground electronic state corresponds to the maximal spin value of 9. The spin density is concentrated on the four Mn atoms (~4 spin units in the electron fractions are on two of them, whereas ~5 on two others). No spin density is present on all other atoms of complex **I**. At the same time the minimal spin

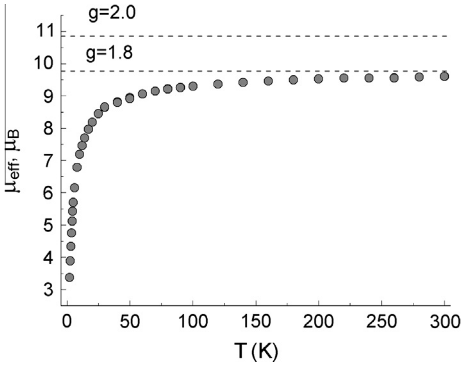


Fig. 2. The temperature dependence of the effective magnetic moment $\mu_{eff} \approx (8\chi T)^{1/2}$ of sample **II**. The dotted horizontal line shows the calculated value of the effective magnetic moment of two Mn^{2+} ($S = 5/2$) ions and two Mn^{3+} ($S = 2$) ions.

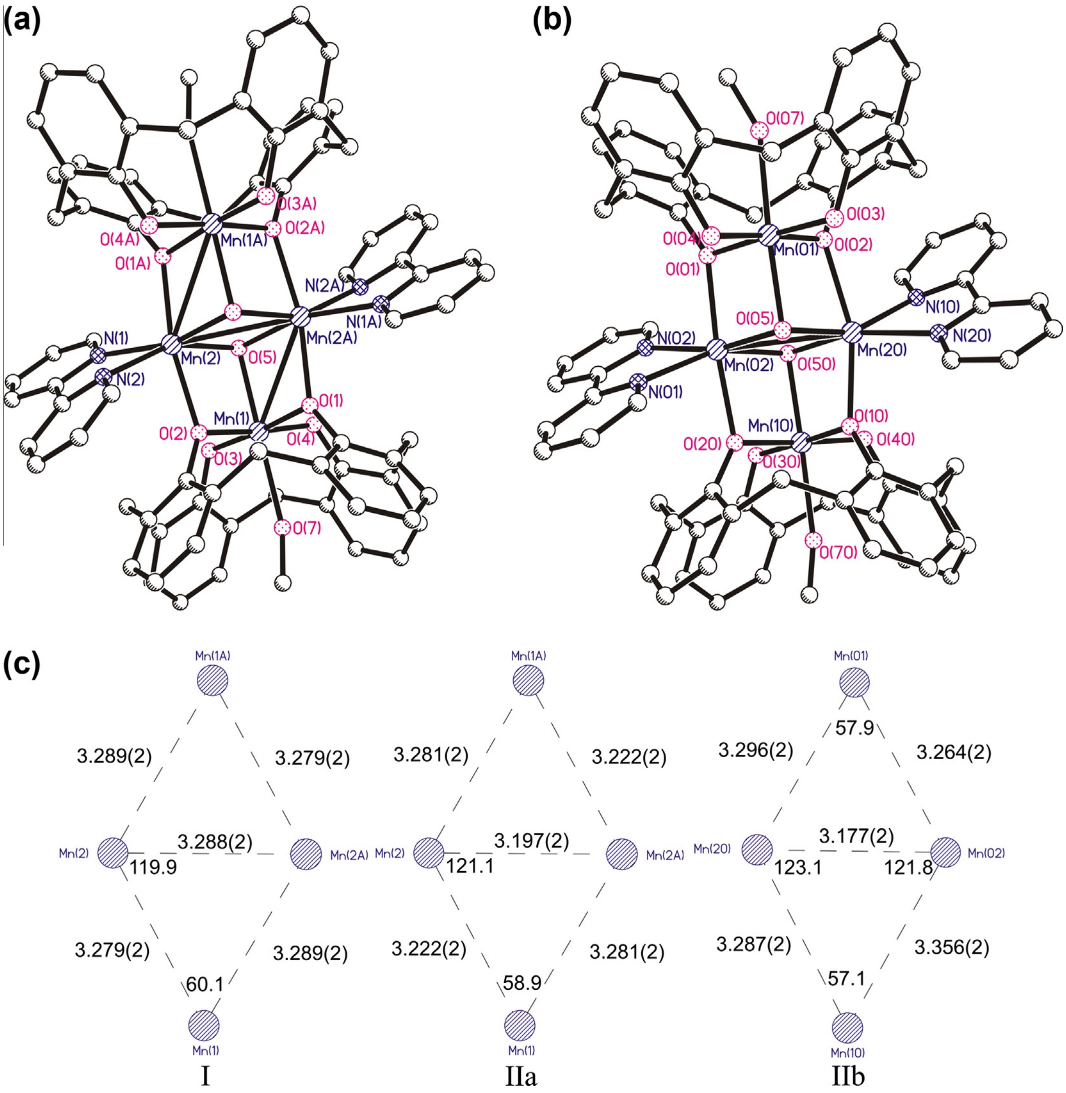


Fig. 1. Structure of metal complex **II** from X-ray data: centrosymmetric (a) and non-centrosymmetric (b). The H atoms are not shown for clarity. Comparison of the structure of the central fragments of metal complexes **I** and **II** (c).