

A water soluble Mn(II) polymer with aqua metal
bridgestCite this: *Dalton Trans.*, 2013, **42**, 7838Received 11th January 2013,
Accepted 12th February 2013

DOI: 10.1039/c3dt00097d

www.rsc.org/dalton

Mònica Fontanet,^a Montserrat Rodríguez,^a Isabel Romero,^{*a} Xavier Fontrodona,^a
Francesc Teixidor,^{*b} Clara Viñas,^b Núria Aliaga-Alcalde^{c,d} and Pavel Matějček^e

The first water soluble and crystallographically determined polynuclear Mn(II) complex, with water molecules bridging every two Mn centers, is reported. This is an unusual feature in 1D oligomer Mn(II) compounds with a nuclearity higher than 2. The polymer structure is largely preserved in water.

Coordination polymers are currently of great interest and represent an active area of coordination chemistry because of their special roles in multiple fields.¹ Also, polynuclear manganese complexes attract great interest owing to their relevance in many important naturally occurring processes.² Regarding organic spacers, carboxylic ligands are frequent choices for metal-organic networks, among other reasons due to their rich modes of coordination.³ With monocarboxylate ligands, dinuclear complexes with the $[\text{Mn}_2(\mu\text{-OH}_2)(\mu_{1,3}\text{-O}_2\text{CR})_2]^{2+}$ core have been reported⁴ and trinuclear compounds have also been described,⁵ the latter being either linear or triangular.⁵ On the other hand, a search in the Cambridge Structural Database (CSD) for the motif $[\text{Mn}_3(\mu_{1,3}\text{-O}_2\text{CR})_6]$ provides a number of trinuclear clusters “Mn₃”, a few dodecanuclear “Mn₁₂” and tetranuclear “Mn₄” complexes and in much less ratio hexanuclear “Mn₆” and heneicosanuclear “Mn₂₁” species. Regarding the trinuclear systems, most are linear. Complexes with μ_2 -oxo, -hydroxo or aqua bridges have not been found in any of the structures studied. Therefore, no nuclearities higher than 21 incorporating the scrutinized motif $[\text{Mn}_3(\mu_{1,3}\text{-O}_2\text{CR})_6]$ have

been found; hence no coordination polymers with this motif have been described until now. The use of carboranes in supramolecular chemistry is a topic that generates great interest for their particular properties⁶ that may induce unconventional characteristics in the supramolecular structures in which they are inserted. In earlier work with the $[\text{1-CO}_2\text{-1,2-closo-C}_2\text{B}_{10}\text{H}_{11}]^-$ ligand and Zn^{II} , Cu^{II} , Ni^{II} and Mo^{II} ions, the geometrical features found in the resulting complexes were not unique to conventional monocarboxylate ligands.⁷ Our vision of the carboranyl substituent, however, is that it provides good space filling, hydrophobicity and electron withdrawing properties, suggesting the possibility of inducing distinct geometrical behavior in polynuclear complexes. If the expected structural change had not been observed, it could be due to the metal ions studied, and their dominant prevalence for a specific nuclearity and arrangement. Mn^{II} is a metal ion that offers different structural possibilities and has never been studied with this kind of ligand. In this work we describe the synthesis in water of the first example of an air-stable polymer of Mn^{II} with water molecules bridging every two Mn^{II} centers. It has been possible using the carboranycarboxylate ligand $[\text{1-CH}_3\text{-2-CO}_2\text{-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}]^-$. Polymer **1** was obtained as a white solid, by mixing a suspension of the acid $\text{1-CH}_3\text{-2-CO}_2\text{H-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}$ and MnCO_3 in a 1 : 1 ratio, in water at 30 °C stirring for 2 h (Fig. 1).

ORTEP plots for the X-ray structure of **1** are presented in Fig. 2a. Polymer **1** displays an unusual feature in 1-D oligomer Mn^{II} complexes with a nuclearity higher than 2 that is the existence of water molecules bridging every two Mn centers. Each of the Mn^{II} centers possesses a distorted octahedral geometry and the ligands are disposed in a zig-zag fashion

^aDepartament de Química and Serveis Tècnics de Recerca, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain. E-mail: marisa.romero@udg.edu; Fax: +34 972 418150; Tel: +34 972 418262

^bInstitut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, E-08193 Bellaterra, Spain. E-mail: teixidor@icmab.es

^cUniversitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain

^dICREA-Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain

^eDepartment of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic

†Electronic supplementary information (ESI) available: Experimental section, spectroscopic and magnetic properties, crystallographic data, DLS. CCDC 907977 and 907978 for complexes **1** and **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00097d

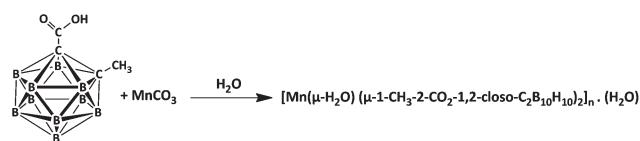


Fig. 1 Synthesis of polymer **1**.

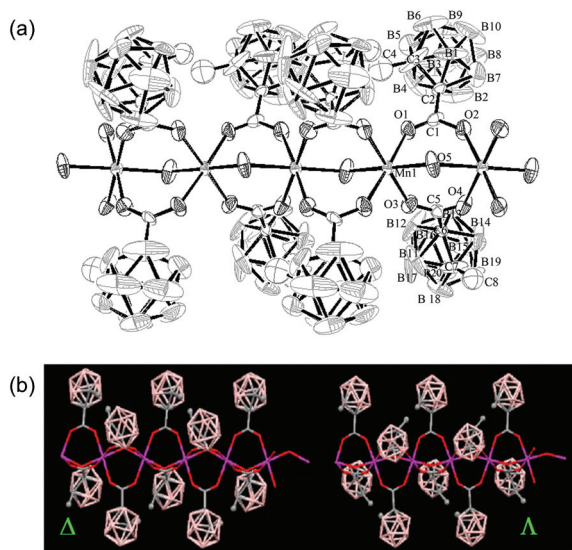


Fig. 2 (a) X-ray structure of polymer **1** showing the monodimensional arrangement. (b) X-ray structure of **1** showing different conformations for the polymeric chains.

through the chain. The bulky nature of the ligand prevents intermolecular interactions among these lineal arrays. Each Mn^{II} atom is coordinated by four carboxylate oxygen atoms and two aqua oxygen atoms and is bridged to other Mn atoms by two carboranilcarboxylate ligands and by an aqua ligand. The two $\mu_{1,3}$ -carboxylate groups are similar, with comparable $\text{Mn}-\text{O}_{\text{carb}}$ distances. The bridging aqua ligand was identified on the basis of the $\text{Mn}-\text{O}$ distances, $\text{Mn}(1)-\text{O}(5)$, 2.338(13) Å and $\text{Mn}(1)-\text{O}(5)\#1$, 2.302(11) Å, which are significantly longer than those in $\mu\text{-O}-\text{Mn}_2^{\text{III}}$ compounds (1.78–1.81 Å),⁸ in the $(\mu\text{-OH}-\text{Mn}^{\text{III}})_n$ polymer (1.89 Å)⁹ and those in previous $\mu\text{-OH}-\text{Mn}_2^{\text{II}}$ molecular systems (2.05–2.09 Å).⁹ The nonbridging water molecules are situated in the cavity formed by the carboranilcarboxylate ligands, and are linked through hydrogen bonds to the coordinated aqua ligand ($\text{O}-\text{H}$, 1.938 and 2.485 Å) (Fig. S1†). The packing structure of the polymer displays polymeric chiral chains because the methyl group of the carboranilcarboxylate ligand is shifted with respect to the center of the coordinated carboxylate group. Then, two different conformations for these chains (λ and δ) can be found (Fig. 2b).

The polymeric structure of **1** is broken in coordinating solvents such as diethyl ether, leading to the first linear trinuclear Mn^{II} complex **2**, with water bridging entities. The structure of this compound (Fig. 3) consists of a linear array of three Mn^{II} . The central $\text{Mn}(2)$, which is located on a crystallographic inversion center, is coordinated octahedrally by four carboxylate oxygen atoms and two aqua oxygen atoms, similar to the Mn^{II} atoms in **1**.

The $\text{Mn}(2)$ is bonded to both terminal $\text{Mn}(1)$ atoms by two carboranilcarboxylate ligands and by an aqua ligand. The two terminal Mn^{II} ions are hexacoordinated and their coordination is completed by one monodentate carboxylate ligand, one

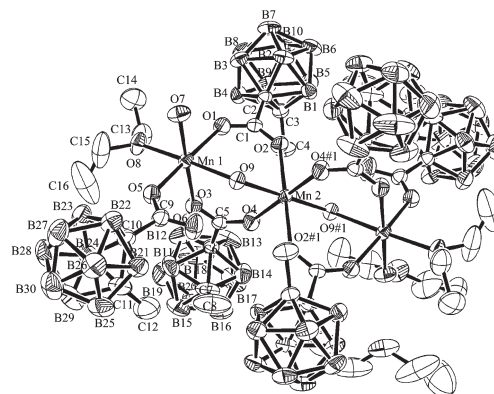


Fig. 3 X-ray structure of trinuclear complex **2**.

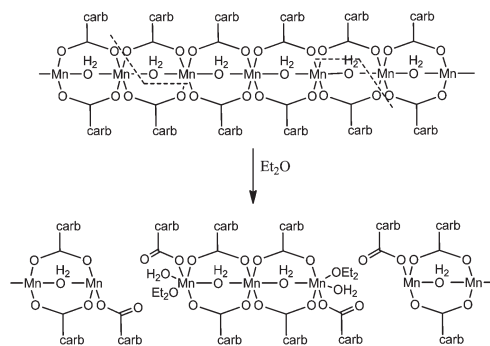


Fig. 4 Cleavage of **1** by Et_2O to yield **2**.

terminal aqua ligand and one oxygen atom from one ether molecule. It is worth noting the existence of two intramolecular hydrogen bonds between the noncoordinating oxygen atom of the carboxylate ligand ($\text{O}6$) and the $\text{H}9\text{A}$ and $\text{H}9\text{B}$ of the bridging aqua ligand ($\text{H}9\text{A}-\text{O}6$, 1.445 Å; $\text{H}9\text{B}-\text{O}6$, 2.714 Å). Another intramolecular weak hydrogen bond is observed between $\text{H}9\text{B}$ and $\text{O}7$ of the terminal aqua ligand, $\text{H}9\text{B}-\text{O}7$, 2.832 Å. Two additional intermolecular H-bonds are formed between the two hydrogen atoms of the terminal aqua ligand and two oxygen atoms from two molecules of diethyl ether ($\text{H}7\text{D}-\text{O}1\text{Y}$, 1.900 Å; $\text{H}7\text{C}-\text{O}1\text{V}$, 2.064 Å).

The clean cleavage of **1** by Et_2O to yield **2** is shown in Fig. 4. In this process only Et_2O and H_2O participate, whereas follow-up cleavage of bridging carboxylates leads to monodentate ligands. Interestingly, terminal Mn atoms in each oligomer remain coordinated to one of the two originally shared (in the polymer structure) carboranilcarboxylate ligands. This clean process of generating oligomers can easily be reversed since removal of the ether solvent quantitatively restores the original polymer in the solid state; this could explain the solubility properties of this Mn polymer in ether by an easy assembling/disassembling process. This reversible process has also been evidenced in solution when using water as the solvent, as will be described below.

Recently, Umena *et al.*¹⁰ have reported the crystal structure of the oxygen-evolving center in photosystem II in which water

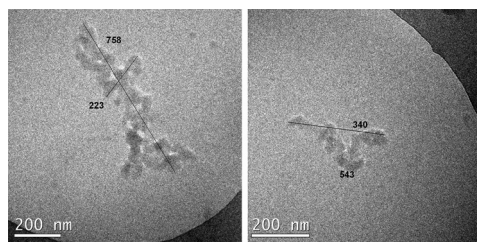


Fig. 5 Cryo-TEM micrograph of a solution of **1** in water.

molecules are bound to the Mn_4CaO_5 cluster. The process described here may provide the opportunity for further design and construction of new supramolecular assemblies as models of the oxygen-evolving center (OEC) and also to understand the role of the water molecules in the catalytic process of water splitting.

Cryo-TEM microscopy analysis of a water solution of **1** corroborated that either a polymeric or aggregate structure exists in solution. The micrographs show a wide range of aggregates with some morphological differences as shown in Fig. 5. Motifs with different lengths (300–700 nm) indicate that a polymer structure or aggregates exist in solution.

Aqueous solutions were analyzed in detail by means of light scattering. It results from these studies that the self-assembly of a polymer in water strongly depends on concentration. In very diluted samples ($c < 0.1 \text{ g L}^{-1}$), the infinite polymer structure is completely broken into fragments smaller than 1 nm. At concentrations higher than 0.1 g L^{-1} , which can be regarded as so-called critical aggregation concentration (CAC), nanoparticles with R_H in the range 200–800 nm were observed. The detection of CAC is quite surprising, because it is not usually the case for other carboranes in water.¹¹ The distribution of R_H is always monomodal but fairly broad at the highest concentrations (Fig. S5†). It is worth noting that the dimensions of the nanoparticles increase with concentration, especially at $c > 10 \text{ g L}^{-1}$. This means that the process does not obey the so-called closed association typical for polymeric micelles and surfactants.¹² The probable explanation is as follows. The further addition of a polymer leads to the elongation of worm-like structures observed by cryo-TEM by the merging of small domains with the larger supramolecular structure. This effect is pronounced at the highest concentrations resembling a transition of surfactant micelles to more complex morphologies like cylinders or lamellae.¹³ However, SAXS/WAXS experiments were not successful and the exact inner structure of the nanoparticles in solution could not be determined. The formation of the fairly large associates is most probably driven by hydrophobicity of carborane clusters and complexation of $[1\text{-CH}_3\text{-2-COO-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}]^-$ to Mn^{II} . The structure is probably swelled by water. Nevertheless, it still retains its organized structure comparable to that in the solid state and can be imagined as the merging of small $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})]_n$ units into worm-like nanoparticles.

In conclusion, with the carboranylcarboxylate ligand uncommon nuclearities and Mn...Mn bridging water units

have been observed for the first time. The aqueous reaction of $1\text{-CH}_3\text{-2-COOH-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}$ with MnCO_3 in a 1 : 1 ratio has led to the first Mn water soluble polymer **1**. The polymeric nature of **1** can be easily fragmented with coordinating solvents, e.g. diethyl ether, generating oligomeric species. In these oligomers the inner Mn...Mn pairs maintain the precise picture found in **1** with the bridging water unit and the two bridging carboxylate ligands while the terminal Mn ions evidence their origin as a result of fragmenting the polymer. Terminal Mn centers in the oligomers contain a monodentate carboranylcarboxylate ligand, one terminal water molecule and one terminal fragmenting solvent, Et_2O in this case. The clean method of fragmentation of the polymer enables a reverse process, allowing the regeneration of the polymer structure. This easy assembling/disassembling process is, most probably, what endows **1** with its notorious solubility properties, and its aggregation concentration dependent ability as shown by the DLS studies. Studies are underway to learn about the effect of a higher positive charge on the stability of the oligomers, and to study the fate of the terminal and bridging water molecules in water oxidation.

We thank the Spanish MINECO (CTQ2010-21532-C02-01, CTQ2010-16237, CTQ2009-06959), Generalitat de Catalunya (2009/SGR/00279) and Ministry of Education and Academy of Sciences of the Czech Republic (MSM0021620857, IAAX00320901) for financial support, and Alexander Jigounov for SAXS/WAXS measurements.

Notes and references

- 1 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117; C. Janiak, *Dalton Trans.*, 2003, 2781; O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; A. K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Commun.*, 2006, 4780; U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626; M. Andruh, *Chem. Commun.*, 2007, 2565; B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207.
- 2 S. Mukhopadhyay, S. K. Mandal, S. Bhaduri and W. H. Armstrong, *Chem. Rev.*, 2004, **104**, 3981; D. C. Weatherburn, S. Mandal, S. Mukhopadhyay, S. Bhaduri and L. F. Lindoy, Manganese, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier Pergamon, Oxford, 2004, vol. 5, p. 1.
- 3 C. Janiak, *Dalton Trans.*, 2003, 2781; X. Lin, J. Jia, P. Hubberstey, M. Schroeder and N. R. Champness, *CrystEngComm*, 2007, **9**, 438; C. L. Cahill, D. T. de Lill and M. Frisch, *CrystEngComm*, 2007, **9**, 15; D. Maspocho, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770.

- 4 S. B. Yu, A. Bino, I. Shweky and S. J. Lippard, *Inorg. Chem.*, 1992, **31**, 3502; A. Caneschi, F. Ferraro, D. Gatteschi, M. Ch. Melandri, P. Rey and R. Sessoli, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1365; B.-H. Ye, T. Mak, I. D. Williams and X. Y. Li, *Chem. Commun.*, 1997, 1813.
- 5 R. L. Rardin, P. Poganiuch, A. Bino, D. P. Goldberg, W. B. Tolman, S. Liu and S. J. Lippard, *J. Am. Chem. Soc.*, 1992, **114**, 5240; M.-H. Zeng, M.-C. Wu, H. Liang, Y.-L. Zhou, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 2007, 46.
- 6 R. N. Grimes, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1289; M. A. Fox and A. K. Hughes, *Coord. Chem. Rev.*, 2004, **248**, 457; H. Jude, H. Disteldorf, S. Fischer, T. Wedge, A. M. Hawkridge, A. M. Arif, M. F. Hawthorne, D. C. Muddiman and P. Stang, *J. Am. Chem. Soc.*, 2005, **127**, 12131.
- 7 O. Kriz, A. L. Rheingold, M. Y. Shang and T. P. Fehlner, *Inorg. Chem.*, 1994, **33**, 3777; M. Fontanet, A. R. Popescu, X. Fontrodona, M. Rodriguez, I. Romero, F. Teixidor, C. Viñas and E. Ruiz, *Chem.-Eur. J.*, 2011, **17**, 13217.
- 8 V. L. Pecoraro, M. J. Baldwin and A. Gelasso, *Chem. Rev.*, 1994, **94**, 807; L. Que Jr. and A. E. Trye, *Prog. Inorg. Chem.*, 1990, **38**, 97.
- 9 D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Polyhedron*, 2003, **22**, 2161.
- 10 Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55.
- 11 P. Matejcek, P. Cigler, K. Prochazka and V. Kral, *Langmuir*, 2006, **22**, 575; P. Matejcek, P. Cigler, A. B. Olejniczak, A. Andrysiak, B. Wojtczak, K. Prochazka and Z. J. Lesnikowski, *Langmuir*, 2008, **24**, 2625; M. Uchman, P. Jurkiewicz, P. Cigler, B. Gruner, M. Hof, K. Prochazka and P. Matejcek, *Langmuir*, 2010, **26**, 6268.
- 12 P. Alexandridis, J. F. Holzwarth and T. A. Hatton, *Macromolecules*, 1994, **27**, 2414.
- 13 A. Bernheim-Groswasser, R. Zana and Y. Talmon, *J. Phys. Chem. B*, 2000, **104**, 4005.