A Mn6 Cluster inside a Mn10 Wheel: Characterization of a Mn16-Oximate Complex Resulting from a Tetrazole-2-pyridylketoneoximate Ligand

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ABSTRACT:

A new Mn16 topology consisting of one hexanuclear \{MnII2MnIII4\} unit coordinated inside a decametallic \{MnII6MnIII2MnIV2\} wheel was synthesized from 2-pyridylcyanoxime and azido ligands. A new tetrazole-2-pyridylketoximate ligand was obtained in situ by cyclization of the cyano group and azide mediated by manganese cations.
Manganese clusters with a \{Mn_{12}O_{12}(RCOO)_{16}\} core have been key compounds in SMM research since its discovery.[1] This core can be envisaged as a MnIV cube inside a MnIII8 wheel, linked by oxo and carboxylato bridges. In search of a SMM response, larger metallic wheels around in-plane defective cubane fragments have been characterized,[2–5] which form a beautiful family of related structures with the easy axis of the MnIII cations roughly aligned (Scheme 1). These larger complexes exhibit lower spin ground states than MnIII8MnIV4 and, except for one of the MnIII10MnIV6 complexes,[3] small magnetization reversal barriers[2,4] or even no SMM response[5] were reported.

Following our studies on the reactivity of 2-pyridyloximes with manganese cations,[6] we have explored new synthetic routes employing the ligand 2-pyridylcyanoxime (pyC{CN}{NO}) (Scheme 2). Air oxidation of Mn(hfacac)2, pyC{CN}{NOH}, Cs(OH), and NaN3 in a 1:1:1:1 ratio in acetonitrile gives the hexadecanuclear complex [MnII8MnIII6MnIV 2(N3)4(pyCOO)2{(CH3COO)2pyC-C{CN}{NO}}10(pyC{Tz}NO)2(O)10]·4MeCN (1·4MeCN), which shows a structural relationship with the above-described MnIII10MnIV 6 complex (Scheme 1). In this work, we present the characterization of complex 1, the study of its magnetic response, and the structural characterization of the new tetrazole-2-pyridylketoneoximate ligand (pyC{Tz}NO2–) (Scheme 2), which is the product of the cyclization reaction between 2-pyridylcyanoxime and azide anions.

Mixed-valent complex 1 contains sixteen manganese atoms linked by means of ten pyC{CN}{NO}– ligands in their η1:η1:η1:μ and η1:η1:η2:μ3 coordination modes, six μ4-O and four μ3-O oxo donors, four end-on azido bridges, four syn-syn carboxylates, and two η1:η1:η1:μ3 pyC{Tz}NO2– ligands (Figure 1). The oxidation states have been assigned on the basis of bond lengths, distortion of the coordination polyhedra, and BVS calculations (Table S1), which results in two tetravalent manganese cations [Mn(5) in an octahedral MnO6 environment], six trivalent manganese cations [Mn(1,2,3) in axially elongated MnO5, MnO5N, and MnO4N2 square-pyramidal or octahedral coordination environments], and eight MnII cations (four of them [Mn(4,6)] in a distorted octahedral environment and four MnO3N4 heptacoordinated cations Mn(7,8)).

The oximato bridges involve all the manganese atoms with a wide range of Mn–N–O–Mn torsions, Table S2. Two azido ligands are coordinated to the external wheel with a Mn(4)–N(19)–Mn(6) bond angle of 93.6(3)° and another two to the inner hexanuclear unit with a Mn(2)–N(22)–Mn(8) bond angle of 110.4(4)°.

Ten manganese cations Mn(3), Mn(4), Mn(5), Mn(6), Mn(7) (and symmetry equivalents) form a \{MnII6MnIII2MnIV2(O)8(N3)2\} wheel around one \{MnII2MnIII4(O)8(N3)2\} defective dicubane fragment. The hexanuclear fragment, composed of the Mn(1), Mn(2), Mn(8) cations (and their symmetry equivalents), is linked to the wheel by means of six μ4-O and additional oximato bridges. The structure of 1 shows closely related fragments with the above-described MnIII10MnIV6 complex,[3,4] but in addition to the different manganese oxidation states, it shows a subunit of the inner defective cubane placed perpendicularly to the mean wheel plane, which generates an unprecedented Mn16 core (Figure 2). It is remarkable that complex 1, together with two Mn16 complexes containing methyl-2-pyridylketoneoximate[7] or 2,6-diacetylpyridineoximate,[8] exhibits the maximum nuclearity seen to date in complexes that have 2-pyridyloxime ligands and is the largest Mn/2-pyridyloximate complex containing azido bridges.[9]

Oximes and oximate–metal species exhibit a wide reactivity without preservation of the (–C–N=O) function.[10] As an example, in pyridylketoxime chemistry, the products of dehydration or rearrangement into amides have often been observed, and, as a consequence, the presence of the pyCOO–/CH3COO– ligands that result from oxidative deoximation promoted by high-valent cations is not rare.[10b] Much more interesting is the unprecedented reactivity of 2-pyridylcyanoximate into the new tetrazole-2-pyridylketoneoximate ligand (Scheme 3). The new pyC{Tz}NO2– ligand shows evident structural similarities with the di-2-pyridylketoximate ligand, but, in this case, the charge is 2–because of the deprotonation of the oximate group and the loss of the tetrazole proton. In 1, the mean pyridine and
tetrazole planes are tilted 34°, and four donor atoms are involved in linking the manganese cations, which, after coordination, forms two five and six-membered chelating rings (Scheme 2).

Although the reaction of nitriles with the azide anion to produce tetrazoles is well known, it requires typically large reaction times (even days) and relatively high temperatures.[11] However, some time ago Ellis and Purcell reported the synthesis of tetrazole that was assisted by CoIII;[12] more recently, several authors have reported that the dipolar addition becomes easier when the reaction is performed on a metallic coordination site: Sharpless et al. reported a synthetic method in the presence of ZnII as catalysts,[13] with reduction of the reaction times to hours at 100 °C, and Henderson et al. reported the room temperature syntheses, assisted by MnII, of several pyridyltetrazoles in 2005.[14] Thus, the presence of the new tetrazole-2-pyridylketoneoximate ligand should be attributed to a similar reaction mediated by the previous coordination of 2-pyridylcyanoximate ligands to one MnII cation and subsequent cycloaddition of one azido anion.

Variable-temperature magnetic susceptibility measurements were performed on powdered samples of 1 under an external field of 0.03 T over the range 2–300 K. The χMT value decreases continuously from 44.1 cm³mol⁻¹K at 300 K and continues to decrease on cooling to 10.0 cm³mol⁻¹K at 2 K, which indicates dominant antiferromagnetic interactions and a low S ground state (Figure 3). The room-temperature value is lower than the spin value of 56.75 cm³mol⁻¹K expected for eight uncoupled MnII (S = 5/2), six MnIII (S = 2) and two MnIV (S = 3/2) ions because of the moderately strong MnII–MnIII and MnII–MnIII antiferromagnetic coupling mediated by the oximate bridges.

The magnetization measurements show a maximum value equivalent to twelve electrons under the maximum field of 5 T. The magnetization still strongly increases under the maximum field and saturation is not achieved because of continuous population of the low-lying larger spin levels under a high external field. From the low temperature χMT value and the slope of the magnetization plot in the lowfield region, an S = 4 ground state appears to be reasonable for 1. The easy axis of the six MnIII cations are roughly parallel, but χ M out-of-phase signals were not found in the AC susceptibility measurements above 2 K, as could be expected for a centrosymmetric cluster (Figure S2).

In conclusion, we have reported a mixed-valent MnII8MnIII6MnIV 2 complex from reaction of the precursor Mn(hfacac)2 with the 2-pyridylcyanoxime and azido ligand in basic medium. The complex exhibits an unprecedented topology consisting of a hexanuclear {MnII2MnIII4} defective cubane unit coordinated inside a decanuclear {MnII6MnIII2MnIV2} wheel. Reaction of 2-pyridylcyanoximate with azido anions, mediated by manganese cations, leads to the characterization of a new member of this family of ligands containing a tetrazole group, which introduces changes in the total charge of the ligand and offers new coordination possibilities. Further attempts to isolate pure tetrazole-2-pyridylketoneoxime are underway.
EXPERIMENTAL SECTION

Physical Measurements: Magnetic susceptibility measurements were carried out on polycrystalline samples by using a Quantum Design MPMS-5 SQUID susceptometer working in the range 2–300 K under magnetic fields of 0.3 T (300–30 K) and 0.03 T (30–2 K) to avoid saturation effects. Diamagnetic corrections were estimated from Pascal tables. Infrared spectra (4000–400 cm$^{-1}$) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer.

Syntheses: Reagents (Sigma–Aldrich Inc.) were used as received. The pyC{CN}NOH ligand was prepared according to the improved[ 15] method reported in the literature.[16]

$[[\text{Mn}_{16}(\text{N}_3)_4(\text{pyCOO})_2(CH_3COO)_2\text{pyC}{\text{CN}}\text{NO}]_{10}(\text{pyC}\{\text{Tz}\text{NO}\})_{2-}(\text{O})_{10}]\cdot 4\text{MeCN}$ ($\text{1}\cdot 4\text{MeCN}$):

($\text{1}\cdot 4\text{MeCN}$) was obtained from the reaction of $[\text{Mn(hfacac)2}]\cdot 3\text{H}_2\text{O}$ (262 mg, 0.5 mmol), pyC{CN}NOH (76 mg, 0.5 mmol) and NaN$_3$ (33 mg, 0.5 mmol) in a basic medium of CsOH (83 mg, 0.5 mmol) in acetonitrile (20 mL) as solvent. After the mixture was stirred in open air for 30 min, the solution became dark brown. Dark crystals (almost black, reddish by transparency) adequate for X-ray diffraction were obtained after a week by crystallization in a closed vial or by layering with diethyl ether; moderate yield (30 %). Dried C$_{100}$H$_{62}$Mn$_{16}$N$_{56}$O$_{30}$ ($\text{1}$) (3406.95) was used for the X-ray crystallographic analysis.

Single-Crystal X-ray Structure Analyses: A black plate-like specimen of C$_{108}$H$_{74}$Mn$_{16}$N$_{60}$O$_{30}$, approximate dimensions 0.070 0.120 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a Mo sealed tube ($\lambda = 0.71073$ Å). The integration of the data using a triclinic unit cell yielded a total of 35261 reflections to a maximum $\theta$ angle of 22.06$^\circ$ (0.95 Å resolution), of which 9766 were independent (average redundancy 3.611, completeness = 99.2 %, $R_{int} = 10.70\%$, $R_{sig} = 13.67\%$) and 5077 (51.99%) were greater than 2$\sigma$(F2). The final cell constants of $a = 14.732(3)$ Å, $b = 17.427(3)$ Å, $c = 18.052(3)$ Å, $\alpha = 63.703(7)^\circ$, $\beta = 84.952(8)^\circ$, $\gamma = 73.532(7)^\circ$, volume = 3980.7(13) Å$^3$ are based upon the refinement of the XYZ-centroids of reflections above 20σ(I). The structure was solved by using the Bruker SHELXTL Software Package and refined by using SHELXL.[17] The unit cell contains one acetonitrile and one water molecule, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. Details of the crystal data and refinement are given in Table S3. CCDC-1028713 (1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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Legends to figures

Scheme 1. Core of MnIII8MnIV4, MnIII9MnIV6, MnIII10MnIV6, and MnIII12MnIV9 complexes consisting of MnIV cubane or defective cubane fragments inside MnIII wheels. Color key: MnIII, dark green; MnIV, firebrick.

Scheme 2. 2-pyridylcyanoxime (top) and 2-pyridyltetrazoleketoxime (bottom) ligands and their coordination modes found in compound 1.

Figure 1. Top: view of the molecular assembly of compound 1. The green bonds emphasize the inner hexanuclear subunit. Bottom: labeled plots of the Mn10 wheel and the Mn6 subunits of 1. Color key: MnII, yellow; MnIII, dark green; MnIV, firebrick; O, red; N, navy blue; C, black.

Figure 2. View of the relative position of the Mn10 wheel and the Mn6 fragment for complex 1.

Scheme 3. Cycloaddition of the azide anion to the nitrile function of the ligand pyC{CN}NO–.

Figure 3. $\chi$MT product vs. $T$ plot for compound 1. Inset: magnetization plot measured at 2 K.
**Scheme 2.**

pyC(CN)NOH

pyC(Tz)NOH
FIGURE 1.
FIGURE 2.
SCHEME 3.

\[
\begin{align*}
\text{N} & : \text{N} : \text{N}^- \\
\text{N} & : \text{C} \equiv \text{N} \\
\text{N} & : \text{O}^- \\
\end{align*}
\]
FIGURE 3.

\[ \chi_M T / \text{cm}^3 \text{ mol}^{-1} \text{ K} \]

\[ T / \text{K} \]

Inset:

\[ M / N_k \]

\[ H / \text{T} \]