Supporting Information

for

New heterometallic pivalate {Fe$_8$Cd} complex as an example of unusual «ferric wheel» molecular self-assembly

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Experimental section

Materials and methods

Commercial reagents and solvents were used for the synthesis: trimethylacetic acid (HPiv, 99 %, «Merck»), KOH ($\geq$ 99 %), Fe(NO$_3$)$_3$·9H$_2$O ($\geq$ 99 %), Cd(NO$_3$)$_2$·4H$_2$O ($\geq$ 99 %), diethyl ether ($\geq$ 99 %), toluene ($\geq$ 99 %), acetonitrile ($\geq$ 99 %), and distilled water. [Fe$_3$O(Piv)$_6$(H$_2$O)$_3$]·HPiv and [Cd(Piv)$_2$] were prepared according to early published.[1]

Sample weights [Fe$_3$O(Piv)$_6$(H$_2$O)$_3$]·HPiv (100 mg, 0.09 mmol) and [Cd(Piv)$_2$] (28 mg, 0.09 mmol) dissolved in Et$_2$O with constant stirring (40 min; r.t.). The precipitated lemon-colored crystals of the [Fe$_8$(Piv)$_{16}${Cd(Piv)$_2$}(μ-OH)$_8$]·Et$_2$O (**1**) were decanted from the solution, washed with cold MeCN (0 °C) and stored in a sealed ampoule. Yield 65 mg (65 % with respect to the initial iron complex). Anal. calc. for C$_{90}$H$_{170}$Fe$_8$CdO$_{44}$ (excluding solvate molecules): C, 42.97; H, 6.81. Found: C, 43.09; H, 7.13; the ratio of metals according to ICP is Fe$_{0.65}$Cd$_{0.07}$. IR (ATR), ν/cm^{-1}: 2964 m, 2930 w, 2870 w, 1703 br. w, 1556 br. vs, 1482 vs, 1459 w, 1419 vs, 1378 vs, 1360 vs 1227 vs, 1123 w, 1032 w, 938 w, 899 w, 786 m, 591 br. m, 507 w, 443 br. m, 434 br. m.

Microprobe analyses were carried out using an Carlo Erba EA 1108 Series CHN Elemental Analyser (Centre of Collective Use of IGIC RAS. Solid); for the analysis on metals we used a mass spectrometric method with inductively coupled plasma (ICP-MS) (Agilent 7500ce; Agilent Technologies Inc., USA).

Synthesis of $[Fe_8(Piv)_{16}\{Cd(Piv)_2\}(\mu\text{-}OH)_8]\cdot Et_2O$ (1)

Samples of HPiv (30 g, 0.29 mol) and KOH (6 g, 0.11 mol) were dissolved in 40 ml of water at 60 °C. To the obtained homogeneous solution, solutions of the salts $Fe(NO_3)_3\cdot 9H_2O$ (10 g, 0.025 mol) and $Cd(NO_3)_2\cdot 4H_2O$ (5 g, 0.016 mol) were added. Stir until an oily layer forms (15 min). The organic layer was separated by decantation from the solution and extracted with diethyl ether. The resulting extract after evaporation of the solvent gave a solid mass, which was washed with MeCN (to remove residual pivalic acid). Yield 19 g (61% in terms of $Fe(NO_3)_3$). To obtain crystals suitable for X-ray structural studies, the obtained crude solid product (100 mg) was recrystallized from diethyl ether (0-3 °C). The precipitated lemon-colored crystals were separated from the solution by decantation, washed with cold MeCN (0 °C), and stored in a sealed ampoule.

For **1**, Anal. calc. for $C_{90}H_{170}Fe_8CdO_{44}$: C, 42.97; H, 6.81 (excluding the Et_2O solvate molecule). Found: C, 43.09; H, 7.13; the ratio of metals according to ICP is $Fe_{0.65}Cd_{0.07}$. IR, ν/cm^{-1} (s = strong, m = medium, w = weak): 2964 m, 2930 w, 2870 w, 1703 br. w, 1556 br. vs, 1482 vs, 1459 w, 1419 vs, 1378 vs, 1360 vs 1227 vs, 1123 w, 1032 w, 938 w, 899 w, 786 m, 591 br. m, 507 w, 443 br. m, 434 br. m.

X-ray data collection and refinement

X-ray diffraction data were collected at 150(1) K on a Bruker diffractometer equipped with a APEX II area-detector (graphite monochromator, ω-scan technique, 0.3° step) using MoKα-radiation (0.71073 Å), resulting in the overall average redundancy of reflections being over 5. The intensity data were integrated by the SAINT program and corrected for absorption and decay using SADABS (semi-empirical from equivalents).[2] The structure was solved by direct methods using SHELXT[3] and refined on F_2 by full-matrix least-squares using SHELXL-2018.[3] All ordered non-hydrogen atoms were refined with anisotropic displacement parameters. All methyl hydrogen atoms were placed in ideal calculated positions with C-H distances equal to 0.980 Å and refined as rotating group in the riding model with relative isotropic displacement parameters taken as $U_{iso}(H) = 1.5U_{eq}(C)$. The analysis of the Fourier density synthesis revealed that cadmium ion is disordered by four positions. The occupancies for all cadmium positions were refined with the constraint (SAMP 1.0) and were equal to 0.375(1), 0.327(1), 0.251(1),

0.047(1). The anisotropic displacement parameters for four possible position of cadmium ion were refined with the EADP constraint. The positions of hydrogen atoms of OH groups were calculated both with the account of O-H…O hydrogen bond formation and presence of the coordination of oxygen atoms with cadmium ion. As the consequence of the cadmium ion disorder for O1M, O2M, O4M and O5M OH groups the disorder of hydrogen atoms by three positions with the occupancies equal to the corresponding occupancies of cadmium ion was proposed. The contribution of the disordered hydrogen atoms of OH groups due to the fourth position of cadmium ion with occupancy 0.047(1) was not taken into consideration. In addition to cadmium ion, the disorder was observed for most of *tert*-butyl groups and solvate molecule of diethyl ester. The disordered fragments were modelled by applying the same anisotropic displacement parameters on similar atoms and by setting similar distances to be equal within the deviation of 0.001 Å. The intensity of reflections 210, 021, 211, 121, 112, 202, 020 were affected by the beam stop, and therefore these reflections were omitted from final steps of the refinement. Crystal data, data collection and structure refinement details are summarized in Table S1. The structure has been deposited at the Cambridge Crystallographic Data Centre with the reference CCDC number 2016931; it also contains the supplementary crystallographic data. These data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data, data collection and structure refinement details.

Parameters	1
Empirical formula	$C_{92.50}H_{176.50}CdFe_8O_{44.50}$
Formula weight	2560.03
T (K)	150
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	30.306(2)
b (Å)	26.652(2)
c (Å)	32.356(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	26134(4)
Z	8(1)
D_{calc} (g·cm^{-3})	1.301
Crystal dimensions (mm)	$0.24 \times 0.13 \times 0.08$
μ (mm^{-3})	1.093
F(000)	10748

θ range for data collection (°)	2.1-27.6
Reflections collected	103362
Independent reflections	29620 [R_{int} = 0.1008]
Observed reflection I>2σ(I)	13826
GOOF	0.979
Final R_1, wR_2 indices I>2σ(I)	0.0815,0.1874
Final R_1, wR_2 indices (all data)	0.1788, 0.2316
Largest diff. peak and hole (e·Å^{-3})	1.753/−1.481

Mössbauer measurements

The ^{57}Fe Mössbauer spectrum was obtained on a Wissel electrodynamic type spectrometer (Germany) at 300 K. The test sample contained «natural» iron, wherein the content of the ^{57}Fe isotope does not exceed 3 wt.%. As a consequence, the magnitude of the Mossbauer effect does not exceed 2 %. The activity of ^{57}Co(Rh) as a source of Mössbauer radiation was 1.1 GBk. The isomer shifts were measured from the centre of the magnetic hyperfine structure (STS) of metallic iron. The spectrum was processed by standard counting and simulation programs for the Mössbauer transition 3/2 → 1/2. Complex processing of Mössbauer spectrum was carried out by the least squares method using LRT programs – N.N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences and WINNORMOS (Germany).

Magnetic measurements

The DC magnetic susceptibility was measured using a Quantum Design magnetometer PPMS-9 in the temperature range between 2 to 300 K at an applied magnetic field of 0.5 T. Magnetic measurements were performed on polycrystalline samples sealed in a polyethylene bag and covered with mineral oil. The magnetic data were corrected for the sample holder and mineral oil contributions and for the intrinsic diamagnetism.

Quantum-chemical calculations

The isotropic magnetic exchange parameters were computed at the crystallographically determined geometry of the {Fe$_8$Cd} cluster within the spin-unrestricted density functional theory (DFT) framework using the Gaussian 09 package[4] and the broken-symmetry (BS) methodology.[5] The scheme proposed by Yamaguchi and co-workers was employed.[6] The state of maximum multiplicity and a set of 21 non-equivalent BS states were considered. The computed $<\hat{S}^2>$ values and energies were used to extract spin correlation functions and isotropic magnetic exchange parameters by solving the corresponding linear equations through a least-squares fitting procedure.[6] The internal stability of all SCF solutions was confirmed by means of the

stability analysis of Seeger and Pople.[7] The B3LYP functional[8] was used throughout in conjunction with the LANL2DZ basis set and associated effective core potential[9] (for Fe and Cd) and Dunning's D95 basis set[10] (for C, O, and H).

Notes and references

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