New Highly Charged Iron(III) Metal–Organic Cube Stabilized by a Bulky Amine

Carlos Cruz, Andrés Igor Vega Carvallo, Evgenia Spodine, Albert Escuer, José F. Marco, Nieves Menéndez, Diego Venegas-Yazigi, and Verónica Paredes-García*

ABSTRACT: In this work, we report a new octanuclear cluster based on FeIII and the ligand 1H-imidazole-4,5-dicarboxylic acid, [Et3NH]12[Fe8(IDC)12]−10DMF·13H2O (1), with a metal core containing eight FeIII connected by only one type of organic ligand. A peak at 573 mJ/z in the mass spectra of the compound suggests the adduct species [[Fe8(IDC)12]+8H]+. By X-ray photoelectron spectroscopy, the oxidation state of the iron cation was confirmed to be 3+, also identifying the presence of a quaternary nitrogen species, which act as a countercation of the anionic metal core [Fe8(IDC)12]−. Mössbauer spectra recorded at different temperatures show an isomer shift and quadrupole splitting parameters that confirm the existence of only FeIII-HS in the structure of 1. X-ray analysis reveals that compound 1 crystallizes in the orthorhombic system space group Ibam, confirming a molecular cluster structure with an almost regular cube as geometry, with the FeIII atoms located at the corners of the cube and connected by μ1-N,2eN′,O′,O″-IDC3 bridges. Additionally, the magnetic measurements reveal a weak antiferromagnetic coupling in the FeIII coordination cluster (J = −3.8 cm−1). To the best of our knowledge, 1 is the first member of the family of cubes assembled with 1H-imidazole-4,5-dicarboxylic acid and FeIII cation, exhibiting high pH stability over a broad pH range, making it an ideal candidate for the design of supramolecular structures and metal–organic frameworks.

1. INTRODUCTION

One of the fascinating fields in coordination chemistry is the research in polynuclear molecular compounds, also called coordination clusters. This type of compound corresponds to molecular entities formed by multiple metal cation arrangement, connected by organic or inorganic ligands. The molecular structure and properties of the coordination cluster are intrinsically related to the nature of the chosen metal center and the interaction between them through the bridging ligands. Then, coordination clusters presenting cations with unpaired electrons are attractive in the field of molecular magnetism. The slow relaxation of the magnetization reported for the disc-shaped MnII11/111 compound, [MnII2(μ-O2CR)6(H2O)6] (R = methyl, phenyl), is a product of the high-spin state and magnetic anisotropy of the paramagnetic centers. Furthermore, two CrIII wheels bridged by acetate and alkoxide ligands, [CrIII10(O2CMe)4(OR)20], show a different magnetic behavior depending on the alkoxide ligand present in the wheel. The authors report that the methoxide ligand favors a ferromagnetic behavior, while the ethoxide ligand favors an antiferromagnetic behavior. Additionally, two mixed-valence coordination clusters [MnIII2IV14O6(HL)10(N3)3(MeO)3(MeOH)4.5(H2O)1.5(OH)0.5](OAc)·10H2O and [Na2MnIII13, MnIVIII13O6(HL)10(OAc)2(H2O)2(OCH3)2(N3)2.5](OAc)·10H2O·2MeOH (HL = 2,6-(hydroxymethyl)phenol), reported in the literature exhibit the magnetocaloric effect at low temperatures due to the large spin, small anisotropy, and high density of low-lying excited states. Research in coordination clusters based on FeIII is interesting in molecular magnetism not only by its rich coordination chemistry but also because this spin carrier can present spin values ranging from 5/2 to 1/2, depending on the coordination environment. These features make these types of compounds attractive for applications like spin switches and magnetic refrigerants.

From a structural viewpoint, the literature reports several FeIII coordination clusters with a wide variety of nucleic acids, topologies, and geometries, such as [Fe9(O2CPh)12(H2O)2] reported by McCusker et al. and [Fe8(μ-O2C(OH)12(tacn))Br·(H2O)]Br·8H2O reported by Wieghardt et al. (O2CPH2 = benzoate; tacn = 1,4,7-triazacyclononane). Both compounds present planar moieties as central cores, constructed by oxides/peroxides anions in the case of Fe6 and oxides/hydroxides anions in Fe8. Using phosphonic acids, Konar et al. obtained [Fe9(μ3-O)2(O2CPH2)]1 −3H2O (H2L = 2,6-(hydroxymethyl)phenol, reported in the literature).
(Me)_1(O_2CCMe_3)_3 and [Fe_{12}(μ_2-O)_{12}(μ_3-O)_{12}(O_2CCPhH_2)]_{16}(4-buPbHPO_4)_n (O_2PbH(Me))_2 = 3,5-dimethylphenyl phosphonate; O_2CCMe_3 = pivalate; O_2CCPH_2 = diphenylacetate; 4-buPbHPO_4 = p-butylibenzyli phosphonate), with Fe_6 and Fe_12 central cores, showing an icoshedral and a double butterfly structure, respectively. Kang et al. reported the mixed-valence (I).

Furthermore, the characterization of the octanuclear cluster was obtained by single-crystal X-ray diffraction, X-ray powder electron spectroscopy (XPS), and other complementary techniques. Furthermore, the characterization of 1 was complemented with Mössbauer spectroscopy, electronic paramagnetic resonance, and magnetic susceptibility measurements.

2. EXPERIMENTAL SECTION

2.1. Synthesis of [Et_3NH]_{12}[Fe_8(IDC)_{12}]·10DMF·13H_2O (1). Caution: The reaction involves the mixture of a moderate amount of triethylamine (Et_3N) and glacial acetic acid (CH_3COOH). Fuming vapors are released, so care must be taken in this procedure.

To a suspension of Fe(acac)_3 (0.5 mmol) and H(IDC) (1 mmol) in a mixture of 10 mL of water and N,N-dimethylformamide (DMF) (1:1 H_2O/DMF), 5 mL of Et_3N was added with constant stirring. After a few minutes, the suspension disappears, and the resulting dissolution changes the initial orange color to a deep red color. After 10 min of stirring, 5 mL of glacial CH_3COOH was added, giving a deep reddish-brown solution, which was left undisturbed for a few weeks, giving yellow prismatic crystals of 1 (Figure S1). MW = 4475.86 g/mol. Yield: 50% based on iron(III) salt. Anal. Calc. for: C_{162}H_{300}N_{46}O_{71}Fe_8: C, 43.35%; H, 6.71%; N, 14.36%; Fe, 9.98%. Found: C, 43.35%; H, 6.71%; N, 14.36%; Fe, 9.98%.

2.2. Physical Measurements. 2.2.1. Elemental Analysis. The quantitative content of C, H, and N was obtained on a Thermos CHNS flash 2000 elemental analyzer using solid-crystalline samples of 1. The quantitative content of Fe was determined using atomic absorption spectroscopy. Three samples of 1 from different batches were measured in triplicate. Solid crystalline samples of 1 were digested in a 0.5% HNO_3 solution, and the iron concentration was measured with a Perkin Elmer PinAAcle 900F atomic absorption spectrophotometer equipped with an acetylene burner using a flux of acetylene: air of 2.51:10 L min^{-1} as an oxidant mixture. An Fe lamp of 248.33 nm wavelength was used with standard solutions in a linear range of 0.1–3.0 mg Fe L^{-1}.

2.2.2. Mass Spectrometry. Mass spectra were measured in a Linear Ion Trap LITQ-XL Thermo Scientific spectrometer and were analyzed with the software MMass 5.5.0. The analysis was carried out in a DMF:H_2O solution of 1 (pH ≈ 6.0) in negative ion mode, scanning in a range of m/z of 150–1500 (Table S2 shows the peak list of the mass spectrum).

2.2.3. Thermogravimetric Analysis. Thermogravimetric (TG) analysis was performed on a Mettler Toledo TGA/DSC STAR system. The samples were introduced in an alumina holder and heated under a nitrogen atmosphere from room temperature to 900 °C at a heating rate of 5 °C/min.

2.2.4. Single-Crystal X-ray Diffraction. A single crystal of 1 was directly selected from the reaction beaker and glued on the tip of a capillary glass using epoxy resin. Scans on the Bruker APEX2 diffractometer confirmed enough crystal quality to perform full recording using X-ray radiation of Mo Kα (λ = 0.71073 Å). The data were reduced by SAINT,

2.2.6. Mössbauer Spectroscopy. The Mössbauer spectra of finely ground crystals of 1 were recorded between 295 and 4.2 K. The measurements were recorded using two 57Co(Rh) γ-ray sources mounted on both ends of an electromagnetic transducer operated in the triangular mode. One of the sources was used for energy calibration with α-Fe (6 μm) foil. The spectra were analyzed by a nonlinear fit using the NORMOS program, and the energy calibration was made using α-Fe (6 μm) foil. Variable
temperatures were obtained with an Oxford Spectromag 4000 M cryostat connected to an ITC-503 Oxford Instruments temperature controller. To avoid saturation effects and optimize the signal-to-noise ratio, the sample thickness was 10 mg of natural Fe cm\(^{-2}\).

2.2.7. Electronic Paramagnetic Resonance. EPR spectra were collected on a Bruker EMX-1572 spectrometer working at 9.39 GHz (X-band) using polycrystalline samples of 1 at 298 K.

2.2.8. Magnetic Measurements. Magnetic measurements were carried out using a Quantum Design Dynacool Physical Properties Measurement System (PPMS) equipped with a vibrating sample magnetometer (VSM). The dc data were collected under externally applied fields of 1 kOe in the 1.8–300 K temperature range. Also, magnetization measurements at the variable field were performed at 1.8, 3, 5, and 8 K from 0 to 90 kOe. The magnetic signal from the sample holder was negligible to affect our data accuracy and was not considered. Diamagnetic corrections (estimated from Pascal constants) were considered. The simulation of the temperature-dependent magnetic susceptibility data was performed by exact diagonalization of the spin Hamiltonian employing the PHI software.

3. RESULTS AND DISCUSSION

3.1. Synthesis. Concerning the synthesis of 1, the organic ligand H\(_2\)IDC can be considered as a polyprotic acid. Depending on the pH of the media, this ligand can be present in the final product with different protonation degrees (Scheme 1).

![Scheme 1. pK\(_a\) Values of the Organic Ligand H\(_2\)IDC](image)

The initial suspension of H\(_2\)IDC in an H\(_2\)O/DMF mixture gave a pH near 3, indicating that the full protonated H\(_2\)IDC should be the predominant species in this media. When triethylamine (Et\(_3\)N; 36 mmol) was added, the pH increased to 11, causing a displacement of the equilibrium to the more reactive ion species HIDC\(^2+\)/IDC\(^3−\), which are now able to coordinate the Fe\(^{III}\) centers. Then, at the end of the reaction, the acidification with glacial acetic acid (87 mmol) decreased the pH of the solution to 4. Regarding the pH fluctuation in the reaction and the different protonation degrees of the H\(_2\)IDC ligand (IDC\(^3−\)/HIDC\(^2+\)/H\(_2\)IDC\(^+\)), it is possible to infer that the assembly of iron(III) with the organic species should generate multiple possibilities for the final formula of Fe\(_8\) cluster. Thus, an anionic [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\), neutral [Fe\(_8\)(HIDC\(_{12}\))] or catonic [Fe\(_8\)(H\(_2\)IDC\(_{12}\))]\(^{12+}\) species could be considered as a product. Considering that the species of the ligand are dependent on the pH, it is reasonable to infer that IDC\(^3−\) anion should be the predominant species at pH = 11 (pK\(_a\) = 11.8), being also able to coordinate the Fe\(^{III}\) cations to give the Fe\(_8\) cluster [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\). Later, the pH decreases to 4, causing the quantitative protonation of Et\(_3\)N (pK\(_a\) = 10.8) needed to induce the crystallization of the anionic cluster, [Fe\(_8\)(IDC\(_{12}\))]\(^{12+}\). The fact that the Fe\(_8\) cluster was assembled under a basic medium and crystallized under a acidic medium can be taken as evidence about the chemical stability of [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\) over a broad pH range.

Figure S2 shows the mass spectrum of 1 obtained by the linear ion trap in the range of 150–1500 m/z. The base peak at 573 m/z correlates very well with the adduct species {[Fe\(_8\)(IDC\(_{12}\))]\(^{+8H}\)}\(^{4+}\). Other adducts species with lower intensities were also identified at 1147, 764, and 458 m/z, which correlate with {[Fe\(_8\)(IDC\(_{12}\))]\(^{+10H}\)}\(^{2+}\), {[Fe\(_8\)(IDC\(_{12}\))]\(^{+9H}\)}\(^{3+}\), and {[Fe\(_8\)(IDC\(_{12}\))]\(^{+7H}\)}\(^{5+}\), respectively. This result corroborates that the anionic species [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\) is the correct representation for the Fe\(_8\) cluster.

3.2. X-ray Single-Crystal Structural Characterization. X-ray single-crystal analysis reveals that 1 corresponds to a discrete octanuclear cluster forming a cubic polyhedron, which crystallizes in the highly symmetric Ibam orthorhombic system (Table 1). Each corner of the cube is occupied by one Fe\(^{III}\).

![Table 1. Crystallographic Refinement Data for 1](image)

Regarding the pH of the media, this anionic species can be taken as evidence about the chemical stability of [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\) over a broad pH range. The empirical formula and molecular weight given in the table consider the counterions and solvate molecules determined by all the analysis techniques used in the experimental section.

![Figure S2](image)

Figure 1a, being the edges organic ligands. Continuous shape measurement (CShM) was used to evaluate the distortion of the cube. The iron moiety was compared with an ideal cube using the SHAPE software \(^{39}\), obtaining a CShM value of 0.004 \(\pm 0.008\). The crystallographic refinement data for 1 are shown in Table 1. The crystal data were obtained by the linear ion trap in the range of 150–1500 m/z. The base peak at 573 m/z correlates very well with the adduct species {[Fe\(_8\)(IDC\(_{12}\))]\(^{+8H}\)}\(^{4+}\). Other adducts species with lower intensities were also identified at 1147, 764, and 458 m/z, which correlate with {[Fe\(_8\)(IDC\(_{12}\))]\(^{+10H}\)}\(^{2+}\), {[Fe\(_8\)(IDC\(_{12}\))]\(^{+9H}\)}\(^{3+}\), and {[Fe\(_8\)(IDC\(_{12}\))]\(^{+7H}\)}\(^{5+}\), respectively. This result corroborates that the anionic species [Fe\(_8\)(IDC\(_{12}\))]\(^{12−}\) is the correct representation for the Fe\(_8\) cluster.

3.2. X-ray Single-Crystal Structural Characterization. X-ray single-crystal analysis reveals that 1 corresponds to a discrete octanuclear cluster forming a cubic polyhedron, which crystallizes in the highly symmetric Ibam orthorhombic system (Table 1). Each corner of the cube is occupied by one Fe\(^{III}\).
acting as the $\mu$-1\kappa^2\text{N}_2\text{O}_2:2\kappa^2\text{N}',\text{O}^\ominus$-IDC$^{3-}$ bis-chelating bridge, leading to an interconnection distance of Fe(1)−Fe(2) = 6.3754(3) Å (Figure 1c). Additionally, each [Fe(IDC)$_2$]$^{2+}$ moiety is chiral, being the handedness of Fe(1) $\Lambda$ and Fe(2) $\Delta$. Because of the $\Lambda$–$\Delta$ alternating arrangement, a centrosymmetric compound is obtained. In compound 1, the Fe–N and Fe–O bond distances are in the range of 2.028(7)−2.093(7) Å and 1.985(6)−2.003(7) Å for Fe(1) and in the range of 2.069(7)−2.098(7) Å and 1.979(7)−2.005(7) Å for Fe(2). Usually, in coordination compounds, the bond distance can be associated with the oxidation and spin state of the cation. For example, Angaridis et al. reported two molecular systems [Fe(3,5-2Bu$_2$salpn)- (MeDCB1)Fe(3,5-2Bu$_2$salpn)] and {[Fe-(3,5-2Bu$_2$salpn)]$_2$(IDCBI)} (3,5-2Bu$_2$salpn = diaminocarboxylic acid) [H$_2$MeDCB1 = 4,5-dicarboxy-1-methyl-1H-imidazole; H$_2$IDCBI = 4,5-dicarboxyimidazole]. Both compounds are based on Fe$^{3+}$ in a high-spin state (HS), having an FeN$_3$O$_3$ environment formed by $\kappa^2\text{N}_2\text{O}^\ominus$-HDCB$^{2-}$/$\kappa^2\text{N}_2\text{O}^\ominus$-MeDCB$^{2-}$ and $\kappa^2\text{O}_2\text{N}_2\text{O}^\ominus$-$\text{S}_5\text{Bu}_2$salpn, being the cations bridged by $\mu$-1\kappa^2\text{N}_2\text{O}_2:2\kappa^2\text{N}',\text{O}^\ominus$-imidazole ligand as in 1 and presenting Fe–N = 2.126(3)−2.107(1) and Fe–O = 1.883(2)−2.223 Å bond distances. Also, in other imidazoles Fe$^{III}$-HS compounds, the average Fe–N is 2.091 Å. All these data permitted us to infer that the Fe(1) and Fe(2) cations present in 1 can be assigned as Fe$^{III}$-HS. Therefore, the iron cluster previously determined from structural X-ray measurements can be represented as [Fe$_8$(IDC)$_{12}$]$^{12-}$.

Figure 1. (a) Molecular structure of 1 and view of the packing through the c axis. (b) Coordination environment of Fe$^{III}$ centers in 1 and (c) $\mu$-1\kappa$^2$\text{N}_2\text{O}_2:2\kappa^2\text{N}',\text{O}^\ominus$ bis-chelating bridge mode of IDC$^{3-}$.

Literature reports different analogous M$_8$-H$_2$IDC$^{n-}$ compounds based on other transition metal cations (2−18), which are summarized in Table 2. For example, Liu et al. obtained under solvothermal conditions an anionic Ni$^{II}$ cluster, [Ni$_8$(IDC)$_{12}$]$^{8-}$ (2). This Ni$_8$ cube is surrounded by a large number of solvent molecules and protonated 4,4′-trimethylenedipiperidinium as counterions. Likewise, by a solvothermal reaction, Xu et al. reported the synthesis of another 0D Ni$^{II}$, neutral cubic cluster [(Ni$_8$(H$_2$IDC)$_{12}$)(HDCBI)]$_2$8(C$_2$H$_5$OH)-18(H$_2$O) (3), in which the H$_2$IDC ligand is found both as di- and monoprotonated species and also surrounded by solvate molecules. Meanwhile, Cheng et al. reported the synthesis at room temperature of another anionic cluster without solvate molecules [Me$_2$Ni]$_{20}$[Co$_6$(IDC)$_{12}$]$_4$ (4), but unfortunately, the crystalline structure was not reported in the publication. Moreover, extended networks obtained from the M$_8$ anionic cluster and stabilized by the incorporation of a second metal cation have also been reported (5−10). In these cases, the imidazole ligand is present in the full deprotonated form (IDC$^{3-}$), giving a cluster with a highly negative charge. For compounds 6−10, the anionic cluster is stabilized by the linkage of alkaline cations to the carboxylate groups belonging to the imidazole ligand. Besides, Cheng et al. reported a mixed-valence Co$^{III}$/Co$^{II}$ cubic cluster forming a 1D heterometallic coordination polymer [Ni(cyclam)]$_n$[Ni(cyclam)- (H$_2$O)$_2$]$_{n-2}$[Ni(cyclam)][Co$_6$(IDC)$_{12}$]$_4$41H$_2$O (5). This extended compound is assembled by the [Co$_6$(IDC)$_{12}$]$^{18-}$ formula of the compound synthesis type dimension charge of the cluster H$_2$IDC species ref

| formula of the compound | synthesis type | dimension | charge of the cluster | H$_2$IDC species | ref |
|-------------------------|---------------|-----------|----------------------|-----------------|-----|
| [Et$_3$NH]$_2$[Fe(IDC)$_2$]$^{2+}$-10DMF-13H$_2$O (1) | R.T.$^a$ | 0D | −12 | IDC$^{3-}$ | this work |
| Ni$_8$(H$_2$IDC)$_{12}$-EtOH$_2$·H$_2$O (2) | solvothermal | 0D | −8 | H$_2$IDC$^{2-}$ | 43 |
| Ni$_8$(H$_2$IDC)$_{12}$·8(C$_2$H$_5$OH)-18(H$_2$O) (3) | solvothermal | 0D | 0 | H$_2$IDC$^{2-}$/HDC$^{2-}$ | 43 |
| [Me$_2$Ni]$_{20}$[Co$_6$(IDC)$_{12}$]$_4$ (4) | R.T. | 1D | −14 | IDC$^{3-}$ | 44 |
| [Ni(cyclam)]$_n$[Ni(cyclam)-H$_2$O$_2$]$_{n-2}$ (5) | R.T. | 1D | −14 | IDC$^{3-}$ | 44 |
| Ni$_8$(H$_2$IDC)$_{12}$·74(H$_2$O) (6) | R.T. | 3D | −20 | IDC$^{3-}$ | 43 |
| K$_2$[Ni$_8$(IDC)$_{12}$]$^{2+}$-50(H$_2$O) (7) | R.T. | 3D | −20 | IDC$^{3-}$ | 43 |
| K$_2$[Ni$_8$(IDC)$_{12}$]$^{2+}$-29(H$_2$O) (8) | R.T. | 3D | −20 | IDC$^{3-}$ | 43 |
| [Ni$_8$(H$_2$IDC)$_{12}$]$^{2+}$-Li$_2$(H$_2$O)$_{10}$ (9) | solvothermal | 3D | −20 | IDC$^{3-}$ | 45 |
| Ni$_8$(H$_2$IDC)$_{12}$-EtOH$_2$·H$_2$O (10) | solvothermal | 3D | −20 | IDC$^{3-}$ | 45 |
| Zn$_8$[guanidinium]$_n$[IDC$_2$](HDCBI)$_2$[DMF]$_2$(H$_2$O)$_6$ (11) | solvothermal | 3D | −16 | H$_2$IDC$^{2-}$/IDC$^{3-}$ | 46 |
| Cd$_8$Na$_2$(H$_2$IDC)$_3$(H$_2$Pip)$_2$(EtOH)$_2$(H$_2$O)$_{12}$ (12) | solvothermal | 3D | −12 | H$_2$IDC$^{2-}$/IDC$^{3-}$ | 46 |
| Cd$_8$K$_2$(H$_2$IDC)$_3$(DFM)$_2$(H$_2$O)$_{16}$ (13) | solvothermal | 3D | −8 | H$_2$IDC$^{2-}$ | 46 |
| Cd$_8$K$_2$(H$_2$IDC)$_3$(DFM)$_2$(H$_2$O)$_{14}$ (14) | solvothermal | 3D | −8 | H$_2$IDC$^{2-}$ | 46 |
| Cd$_8$K$_2$(H$_2$IDC)$_3$(DFM)$_2$(H$_2$O)$_{15}$ (15) | solvothermal | 3D | −8 | H$_2$IDC$^{2-}$ | 46 |
| Mn$_8$K$_2$(H$_2$IDC)$_3$(DFM)$_2$(H$_2$O)$_{16}$ (16) | solvothermal | 3D | −8 | H$_2$IDC$^{2-}$ | 46 |
| [Cr$_3$(H$_2$IDC)$_2$]-H$_2$O (17) | solvothermal | 0D | 0 | H$_2$IDC$^{2-}$ | 47 |
| [Cr$_3$(H$_2$IDC)$_2$]-H$_2$O (18) | solvothermal | 0D | 0 | H$_2$IDC$^{2-}$ | 47 |

$^a$H$_2$TMDP$^{2+}$ = 4,4′-trimethylenedipiperidinium. $^b$Me$_2$Ni$^+$ = tetramethylammonium, crystalline structure not reported. $^c$cyclam = 1,4,8,11-tetraazacyclotetradecane. $^d$H$_2$Pip$^{2+}$ = piperazinium. R.T. = room temperature.
cluster, which is coordinated by the carboxylate group to the \([\text{Ni}^{2+}\text{cyclam}]^{2+}\) complexes.

On the other hand, Alkordi et al. reported six 3D networks built from \(M^{11}\) anionic cubes \((11−16)\). Zein, \(\text{Zn}_{12}\)(guanidinium)\((\text{HIDC})_4\)(DMF)\((\text{H}_2\text{O})_3\) \(11\) and \(\text{Cd}_{3}\text{Na}_8\)(HIDC)\((\text{HIDC})_4\)(\(\text{H}_2\text{Pip}\))\((\text{EtOH})_2\)(\(\text{H}_2\text{O})_7\). \(12\) contain HIDC\(^{2−}\) and IDC\(^{−}\) species as ligands. In the case of \(11\), the negative charge is balanced by both guanidinium and zinc cations, being the zinc cations also coordinating the carboxylates belonging to the anionic cubes originating in this form the 3D structure. For \(12\), sodium and a protonated amine (piperazinium) are also balancing the charge of the cubic cluster. The authors also report a series of compounds \(M_{12}\)(HIDC)\(_{12}\)(DMF)\(_3\)(\(\text{H}_2\text{O})_6\) \(\text{M} = \text{Zn}, \text{Cd}, \text{Co}^{2+}\), and \(\text{Mn}^{2+}\) \((13−16)\), containing only the HIDC\(^{2−}\) species as a ligand, but in these cases, only alkaline cations are stabilizing the \([\text{M}_9\text{HIDC}]^{18−}\) cluster in the 3D networks. The two last examples \((17\) and \(18)\) were reported by Zhai et al. and correspond to \(\text{In}^{11+}\text{Cr}^{11+}\) heterometallic OD cubes \([\text{Cr}_2\text{In}_6\text{HIDC}]^{12−}\text{H}_2\text{O}\) and \([\text{Cr}_{12}\text{In}_{18}\text{HIDC}]^{12−}\text{H}_2\text{O}\), being neutral species and only including the HIDC\(^{2−}\) in the structure.

In our case, although the molecular structure of the \(\text{Fe}_8\) core was well identified by X-ray single-crystal analysis due to the size of the cluster and the high symmetry of the cell, part of the electronic density surrounding the cluster remained invisible for this technique, as has also been reported in an analogous cobalt octanuclear cluster. However, according to the examples mentioned above, the full deprotonated IDC\(^{−}\) species generates \(M_{12}\) cubes with the highest negative charge, which is stabilized by other metal cations or bulky protonated amines. Then, 12 counterions must be present in the compound to neutralize the negative charge of the resulting \([\text{Fe}_8\text{HIDC}]^{12−}\) cluster. Since no additional iron centers were found in the intercluster space, only the triethylammonium cation should be acting as a counterion. This counterion also provides enough steric hindrance to avoid the assembly between the iron clusters, thus producing a molecular crystal packing for \(1\), as was also reported for the \(\text{Ni}_4\) analogous system with 4,4′-trimethylene-dipiperidinium. Accordingly, XPS, TG, and FTIR were performed to complement the structural characterization.

3.3. XPS. To gather more information about the chemical composition of \(1\), \(\text{Fe}_2\) \(\text{N}_1\) \(\text{C}_1\), and \(\text{O}_1\) high-resolution XPS spectra were also collected (Figure 2a). The XPS spectrum consists of an asymmetric spin-orbit doublet with binding energies of the Fe \(2p_{3/2}\) and Fe \(2p_{1/2}\) core levels of 711.5 and 725.2 eV, respectively, and a small shake-up satellite at 717.8 eV. The shape of the spectrum, the binding energies of its different components, and the presence of the small satellite are all characteristic of iron in 3+ oxidation state and high-spin configuration, confirming the observation in the structural characterization. The N 1s spectrum was best-fitted to two contributions. The major one, located at a binding energy of 398.7 eV, can be ascribed to an amine-type or aromatic-type N–H bond belonging to the imidazole ring of the organic ligand. The higher binding energy component at 401.1 eV is characteristic of a quaternary nitrogen species, which must belong to the triethylammonium \((\text{Et}_3\text{NH})^+\) present in the intercluster space of \(1\) acting as a counterion. A fit considering also the contribution to the N 1s spectrum of a ternary amine was not successful, discarding the presence of trimethylamine in the final product. The C 1s spectrum contains three different carbon species at 284.6, 285.8, and 288.4 eV, which can be associated with C–C or C–H bonds; C–N, C–O, C≡N, or C≡N bonds; and O–C≡O bonds, respectively. The O 1s spectrum contains three contributions. The main one at 531.4 eV can be associated with C≡O bonds in O≡C–O groups, while the second one at 533.0 eV may correspond to C–O bonds in O=C–O groups. The minor component at 535.0 eV might be ascribed to a small oxygen satellite. All the identified bonds are part of the IDC\(^{−}\) anionic ligand present in the cluster \([\text{Fe}_8\text{HIDC}]^{12−}\). Nevertheless, from a...
Figure 3. (a) Plots of $\chi_m$ vs $T$ and $\chi_m^{-1}$ vs $T$ for 1. (b) Images of magnetic pathways for the Fe$_8$ moiety in 1 and the binuclear Fe$_2$ simplified model.

chemical viewpoint, the presence of a quaternary nitrogen species corroborates that triethylammonium (Et$_3$NH$^+$) is the countercation of the anionic iron cluster, which is also consistent with the reaction condition used to obtain 1. Therefore, the molecular structure of the iron cluster is deduced to be [Et$_3$NH]$_{12}$[Fe$_8$(IDC)$_{12}$].

An important fact that was found during the development of this work is that the sample is very sensitive to the irradiation by the X-rays of the XPS spectrometer and that it undergoes important chemical changes after relatively short irradiation times. To minimize the occurrence of these changes, we used a low power in the X-ray gun (100 W against the more usual 300 W) and slightly higher pass energy (30 eV vs the usual 20 eV) to record the data. Using a constant pass energy of 30 eV instead of 20 eV allows recording the spectra with a larger number of counts in a given time without compromising too much the energy resolution. So, for the Fe 2p spectrum shown in Figure 2b, we used only one scan (less than 5 min of irradiation) since increasing the number of scans can lead to chemical changes. Figure 2b collects the Fe 2p spectra recorded after several increasing irradiation times. It is evident that, even after short irradiation times (see spectra (b) and (c) in Figure 2b), the lines of the Fe 2p spectrum shift to lower binding energies and a strong shake-up satellite starts developing at around 714 eV. These results clearly indicate that the initial Fe$^{II}$-HS is progressively reduced to an Fe$^{II}$-HS species upon X-ray irradiation. In fact, the spectra recorded at intermediate irradiation times contain both Fe$^{II}$-HS/Fe$^{III}$-HS contributions. After long irradiation times (Figure 2b), the Fe 2p spectrum only shows the presence of Fe$^{III}$-HS species. Important changes are also observed in the N 1s spectra 2c. In this case, a decrease in the intensity of the protonated Et$_3$NH$^+$ species is observed upon X-ray irradiation. However, and contrary to the iron core, the quaternary nitrogen species appears to be more resilient, as it is still present after long irradiation times. The mechanisms giving place to chemical changes under X-ray irradiation in XPS are complex and have been commented in detail elsewhere. In particular, in the case of the reduction of metal cations in oxides, interionic Auger decay processes appear to play an important role. Among all the chemical changes reported, the degradation of quaternary nitrogen species (deprotonation) has also been reported for some organic compounds. The results are relevant because they stress the need of being extremely careful when recording XPS data for this type of compound. Otherwise, erroneous conclusions can be drawn from the recorded data.

3.4. FTIR and Thermogravimetric Measurements. Figure S3a,b shows the infrared spectra of 1, compared with those of trimethylamine in acidic media and N,N-dimethylformamide. A clear match of the first two spectra between 3000 and 2400 cm$^{-1}$ can be observed, in agreement with the presence of the cationic Et$_3$NH$^+$ species in 1 (Figure S3a). Also, the strong absorption at 1680 cm$^{-1}$ (observed in the spectrum of 1) is exactly in the same position of the C$=$O vibration associated with DMF molecules (Figure S3b), indicating that this molecule must also be present in the final formula. Additionally, thermogravimetric analysis was performed under a nitrogen atmosphere (Figure S4) to characterize the presence of solvent molecules and thermal stability of 1. The cluster is stable until 250 $^\circ$C, showing two weight losses of 5.2% (30–90 $^\circ$C) and 16.1% (190–250 $^\circ$C) associated with solvate molecules. Considering that both H$_2$O and DMF were used as a solvent in the synthesis of 1 and as it has been reported for other compounds, it is reasonable to assign the first loss to the release of 13 water molecules (5.2%) and the second one to 10 DMF molecules (16.3%). At higher temperatures, a third weight loss of 30.2% (250–360 $^\circ$C) is observed. Literature data show that triethylammonium salts (triethylammonium bis-7,7,8,8-tetracyanoquinodimethane) have a thermal decomposition process between 195 and 220 $^\circ$C. Additionally, the inorganic cluster ([([HTEA])_4(TEA)_5]_1[PSb$_{11}$Mo$_3$Mo$_3$O$_{40}$]) shows a continuous weight loss (14.6%) between 44 and 573 $^\circ$C, which is attributed by the authors to the release of triethylamine. Therefore, the loss of 30.2% can be associated to the release of 12 trimethylamine (27.4%) belonging to 12 Et$_3$NH$^+$ acting as counterions. Considering the solvate molecules, the final formula of 1 is [Et$_3$NH]$_{12}$[Fe$_8$(IDC)$_{12}$]-10DMF-13H$_2$O, which correlates very well with the elemental analysis given in the experimental section (section 2.1.1). With these results in mind, Mössbauer spectroscopy, electronic paramagnetic resonance,
antiferromagnetic behavior is the predominant phenomenon at 1.8 K. Clearly, the susceptibility data shows that an increase in the \( \chi_m \) value as the temperature is lowered, leading to a maximum of 0.3 emu mol\(^{-1}\) at 50 K. From this temperature, a constant decrease is observed, leading to a zero value of 0.2 emu mol\(^{-1}\) at 1.8 K. On the other hand, the \( \chi_m^{-1} \) vs T plot gives C and \( \theta \) values of 44.6 emu mol\(^{-1}\) and \(-73.2\) K, respectively. Furthermore, a 35.5 emu K mol\(^{-1}\) value is obtained at room temperature (4.44 emu K mol\(^{-1}\) per Fe\(^{III}\) center) from the \( \chi_m^{-1} \) vs T plot (Figure S5b), close to the expected for eight non-interacting Fe\(^{III}\)-HS centers, 35.65 emu K mol\(^{-1}\) considering \( S_{Fe} = 5/2 \) and \( g = 2.016 \). Lowering the temperature, the \( \chi_m^{-1} \) product constantly decreases as the temperature reaches 100 K. Below this temperature, a more pronounced decrease is observed, reaching a minimum value of 0.3 emu K mol\(^{-1}\) at 1.8 K. Clearly, the susceptibility data shows that an antiferromagnetic behavior is the predominant phenomenon of the Fe\(^{III}\) coordination cluster. Field-dependent magnetization measurements were performed at 1.8, 3, 5, and 8 K and represented as \( N_{Fe} \) vs H and \( N_{Fe} \) vs \( HT^{-1} \) plots (Figure S6). The curves \( N_{Fe} \) vs H show a lack of saturation at the studied conditions, leading to a maximum near 4 \( \mu_B \) at 90 kOe, very far than the value expected for eight Fe\(^{III}\) cations in high spin (40 \( \mu_B \)). For an antiferromagnetic system with a spin state of \( S = 0 \) at low temperatures, the observed magnetization only can belong from non-zero spin states that are close to the ground state. Then, the absence of saturation and the small values obtained for the magnetization corroborate that antiferromagnetic interactions predominate in the Fe\(^{III}\) coordination cluster at low temperatures.

As Figure 3 shows, 12 equivalent \( \mu-1\chi^2N_2O:2x^2N',O' \) magnetic pathways can be established (the edges of the cube) between the eight Fe\(^{III}\)-HS in the octanuclear molecular structure of 1, leading to the following spin Hamiltonian:

\[
\tilde{H}_J = -J S_{Fe1} S_{Fe2} - J S_{Fe1} S_{Fe3} - J S_{Fe1} S_{Fe4} - J S_{Fe1} S_{Fe5} - J S_{Fe2} S_{Fe6} - J S_{Fe2} S_{Fe7} - J S_{Fe2} S_{Fe8} - J S_{Fe2} S_{Fe9} - J S_{Fe3} S_{Fe5} - J S_{Fe3} S_{Fe6} - J S_{Fe3} S_{Fe7} - J S_{Fe3} S_{Fe8} - J S_{Fe4} S_{Fe6} - J S_{Fe4} S_{Fe7} - J S_{Fe4} S_{Fe8} - J S_{Fe4} S_{Fe9} - J S_{Fe5} S_{Fe6} - J S_{Fe5} S_{Fe7} - J S_{Fe5} S_{Fe8} - J S_{Fe5} S_{Fe9} - J S_{Fe6} S_{Fe7} - J S_{Fe6} S_{Fe8} - J S_{Fe6} S_{Fe9} - J S_{Fe7} S_{Fe8} - J S_{Fe7} S_{Fe9} - J S_{Fe8} S_{Fe9}.
\]

No analytical model has been developed for such a complex system. For this reason, the use of a simplified model was necessary. Considering the symmetry of the cluster, the cubic system can be simplified to a binuclear system that consists in two Fe\(^{III}\)-HS cations, connected by a single \( \mu-1\chi^2N_2O:2x^2N',O' \) bridge (Figure 3b), leading to the following spin Hamiltonian:

\[
\tilde{H}_J = -J S_{Fe1} S_{Fe2}.
\]

A fit of the experimental susceptibility data by matrix diagonalization using the \( \tilde{H}_J \) spin Hamiltonian using the PH1\(^{36}\) software was performed between 300 and 1.8 K, considering \( S_{Fe} = 5/2 \) and maintaining the \( g \) factor fixed to the experimental value obtained by EPR, \( g = 2.016 \) (Figure 4). A magnetic coupling constant of \( J = -3.8 \text{ cm}^{-1} \) was obtained, with an agreement factor of \( R = 8.5 \times 10^{-3} = (\Sigma(\chi_m(T_{obs}) - (\chi_m(T_{exp}))^2)/\Sigma(\chi_m(T_{obs}))^2) \). The use of a \( g \) value gave a better fit \( (\chi_m(T_{obs}) - (\chi_m(T_{exp}))^2) \). The interaction between Fe\(^{III}\)-HS/Fe\(^{III}\)-HS can be rationalized considering the five magnetic orbitals associated with Fe\(^{III}\)-HS in an octahedral environment (two \( e_g \) and three \( t_{2g} \)). Thus, the interaction through the IDC\(^3+\) ligand generates a greater possibility of overlapping between the five orbitals of each Fe\(^{III}\)-HS center.\(^{78}\) The fact that the binuclear model presents a rather moderate fit of the magnetic behavior can be explained on the base of the crude simplification of the octanuclear structure of 1. An analogous Ni\(^{II}\) cluster was reported by Liu et al.,\(^{32}\) (H\(_2\)TMDDP)\(_4\)(DMF)\(_4\)(EtOH)\(_4\)·(H\(_2\)O)\(_6\)[Ni\(_8\)(HImDC)]\(_{12}\) (DMF = N,N\-'dimethylformamide, EtOH = ethanol, and H\(_2\)TMDDP = 4,4\-'trimethylene-dipiperidinium), having the same cubic structure of 1 and the same \( \mu-1\chi^2N_2O:2x^2N',O' \) connectivity between the metal cations. This compound also presents an antiferromagnetic behavior, with an identical \( \chi_m \) vs T tendency compared with 1. Although no exchange coupling values were given for this Ni\(_8\) cluster, the example suggests that the bulk magnetic properties of such cubic systems are related not only with the particular magnetic interactions of the metal cations through \( \mu-1\chi^2N_2O:2x^2N',O' \) but also with the spin topology arrangement within the whole cluster structure. In any case, more experimental and theoretical analyses should be performed to clarify the magnetic behavior of compound 1, perhaps studying the orbitals involved in each magnetic exchange pathway and the role of the topology of the cluster in the bulk magnetic properties.

## 3.6. Mössbauer Spectroscopy

The temperature evolution of the Mössbauer spectra of 1 at 295, 77, and 4.2 K is shown in Figure S5. In the studied temperature range, each spectrum consists of a doublet, corroborating that Fe(1) and Fe(2)
4. CONCLUSIONS

A new iron octanuclear coordination cluster was successfully synthesized under an acid–base reaction using a single ligand, 1H-imidazole-4,5-dicarboxylic acid (HIDC). The cluster [Fe8(IDC)12]12− is formed in basic media and crystallized in acid media, proving the chemical stability of the anionic Fe8 cluster in a wide pH range. On the other hand, XPS is a very powerful technique that permitted to identify the existence of triethylammonium cations as a charge compensator that balance the charge of the anionic cluster, and to corroborate the chemical identity of the cluster [Fe8(IDC)12]12− determined by single-crystal X-ray diffraction. Moreover, it was possible to identify that a reduction process centered on the metal cation is produced under experimental conditions of the XPS technique. In fact, the recorded data have to be carefully analyzed to obtain the correct information on the oxidation state of the metal cation in this type of compound. Additionally, Mössbauer spectroscopy corroborated the spin and oxidation state of the iron center within the cluster, leaving no doubt that only FeIII-HS ions are present in the structure of 1. The performed magnetic measurements revealed that weak antiferromagnetic coupling is dominant in the whole temperature range. Although the literature reports the existence of MnII, NiII, CoII/III, ZnII, and CrIII-InIII negative or neutral cubic analogous systems forming 0D, 1D, or 3D compounds with either H2IDC−/HIDC2−/IDC− anionic species, compound 1 is the first member of this family based on FeIII. Despite the challenges presented for the characterization of 1, the present work collects a complete chemical and physical description of a new FeIII-HS coordination cluster with a novel cubic structure.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02420.

Image of the yellow prismatic crystals of 1 (Figure S1); mass spectra (Figure S2); FTIR spectra (Figure S3); TG in the N2 atmosphere (Figure S4); EPR spectra, χ(T) vs T at 1 kOe; best-fit curve at 1 kOe (Figure S5); N(T) vs H and N(T) vs HT−1 plot (Figure S6); complete crystal data and structure (Table S1); peak list of mass spectra (Table S2); and results of CShM calculation (Tables S3–S5) (PDF)

Crystal data and structure refinement for 1 (CIF)

**AUTHOR INFORMATION**

Corresponding Author

Verónica Paredes-García – Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, 8370146 Santiago, Chile; CEDENNA, 8380494 Santiago, Chile; orcid.org/0000-0002-7537-7430; Phone: +56-2-26615756; Email: v paredes@unab.cl

Authors

Carlos Cruz – Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, 8370146 Santiago, Chile; CEDENNA, 8380494 Santiago, Chile

Andrés Igor Vega Carvallo – Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, 8370146 Santiago, Chile; CEDENNA, 8380494 Santiago, Chile; orcid.org/0000-0001-6501-4161

Evgenia Spodine – CEDENNA, 8380494 Santiago, Chile; Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Inorgánica y Analítica, Universidad de Chile, 8380492 Santiago, Chile

Albert Escuer – Departament de Química Inorgànica, Universitat de Barcelona, 08028 Barcelona, Spain; orcid.org/0000-0002-6274-6866

José F. Marco – Instituto de Química Física Rocasolano, 28013 Madrid, Spain

Nieves Menéndez – Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain
Diego Venegas-Yazigi — CEDENNA, 8380494 Santiago, Chile; Facultad de Química y Biología, Departamento de Química de los Materiales, Universidad de Santiago de Chile, 9170022 Santiago, Chile; orcid.org/0000-0001-7816-2841

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02420

Notes

The authors declare no competing financial interest. Accession code CCDC 1810846 contains the supplementary cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ACKNOWLEDGMENTS

The authors acknowledge FONDECYT 1170887, Proyecto Anillo CONICYT ACT 1404 grant, CONICYT-FONDEQUIP/PPMS/EQM130086, CONICYT-FONDEQUIP/EQM140060, Chilean-French International Associated Laboratory for Multifunctional Molecules, and Materials LIAM3-CNRS N°1027 for financial support. The authors also acknowledge Financiamiento Basal, AFB180001, CEDENNA and Laboratory of Analyzes of Solids (L.A.-UNAB). JFM acknowledges financial support from the Spanish Agencia Estatal de Investigación (AEI) through Project No. RTI2018-095303-B-C51 and the Comunidad de Madrid through Project. NANOMAGCOST-CM P2018-NMT-4321. NM acknowledges Agencia Estatal de Investigación Española PGC2018-095642-B-100 proyect.

REFERENCES

(1) Cronin, L.; Fielden, J. Coordination Clusters. In Encyclopedia of Supramolecular Chemistry; 1st ed.; Atwood, J. L. Ed.; Taylor and Francis: London, Published online 2007; 1–10, DOI: 10.1081/ESMC-120024346.

(2) Kostakis, G. E.; Powell, A. K. An Approach to Describing the Topology of Polyonuclear Clusters. Coord. Chem. Rev. 2009, 253, 2686–2697.

(3) Sivaramakrishna, A.; Clayton, H. S.; Makhubela, B. C. E.; Moss, J. R. Platinum Based Mixed-Metal Clusters (PmmM(CO)xLy, M = Ru or Os; n = m = 2 to 10 and Ly = Other Ligands)-Synthesis, Structure, Reactivity and Applications. Coord. Chem. Rev. 2008, 252, 1460–1485.

(4) Kostakis, G. E.; Perlepes, S. P.; Blatov, V. A.; Proserpio, D. M.; Powell, A. K. High-Nuclearity Cobalt Coordination Clusters: Synthetic, Topological and Magnetic Aspects. Coord. Chem. Rev. 2012, 256, 1246–1278.

(5) Beltran, L. M. C.; Long, J. R. Directed Assembly of Metal-Cyanide Cluster Magnets. Acc. Chem. Res. 2005, 38, 325–334.

(6) Peng, J.-B.; Zhang, Q.-C.; Kong, X.-J.; Zheng, Y.-Z.; Ren, Y.-P.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S.; Zheng, Z. High-Nuclearity 3d4f Clusters as Enhanced Magnetic Coolers and Molecular Magnets. J. Am. Chem. Soc. 2012, 134, 3314–3317.

(7) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. Polyoxometalates: Very Large Clusters Nanoscale Magnets. Chem. Rev. 1998, 98, 239–272.

(8) Zhang, S.; Cheng, P. Coordination-Cluster-Based Molecular Magnetic Refrigerants. Chem. Rev. 2016, 16, 2077–2126.

(9) Sessoli, R.; Tsal, H. T.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. High-Spin Molecules: [Mn12O12(μ3-O)2(Cr)12(μ2-OH)12(H2O)]6+. J. Am. Chem. Soc. 1993, 115, 1804–1816.

(10) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic Bistability in a Metal-Ion Cluster. Nature 1993, 365, 141–143.

(11) McInnes, E. J. L.; Anson, C.; Powell, A. K.; Thomson, A. J.; Pousseureau, S.; Sensoli, R. Solvothermal Synthesis of [(Cr9O8(O2CMe)10(μ-OR)3)2] ‘Chromatic Wheels’ with Antiferromagnetic (R = Et) and Ferromagnetic (R = Me) Cr(III)–Cr(III) Interactions. Chem. Commun. 2001, 10, 89–90.

(12) Liu, J.-L.; Leng, J.-D.; Lin, Z.; Tong, M.-L. Ferromagnetic Homometallic Mn10 Cluster and Heterometallic Na2Mn13 Cluster with Large Spin State as Magnetic Refrigerants. Chem. – Asian J. 2011, 6, 1007–1010.

(13) Goura, J.; Chandrasekhar, V. Molecular Metal Phosphonates. Chem. Rev. 2015, 115, 6854–6965.

(14) Kitashima, R.; Imatomi, S.; Yamada, M.; Matsumoto, N.; Maeda, Y. Gradual Two-step Spin Crossover Behavior of Binuclear Iron(III) Complex Bridged by trans-1,2-Bis(4-pyridyl)ethylene. Chem. Lett. 2005, 34, 1388–1389.

(15) Sheikh, J. A.; Jena, H. S.; Clearefield, A.; Konar, S. Phosphonate Based High Nuclearity Magnetic Cages. Acc. Chem. Res. 2016, 49, 1093–1103.

(16) Evangelisti, M.; Candini, A.; Ghirri, A.; Affronte, M.; Pligkos, S.; Brechin, E. K.; McInnes, E. J. L. Molecular Nanoclusters as Magnetic Refrigerants: The Case of Fe14 with Very Large Spin Ground-State. Polyhedron 2005, 24, 2573–2578.

(17) McCusker, J. K.; Christmas, C. A.; Hagen, P. M.; Chadha, R. K.; Harvey, D. F.; Hendrickson, D. N. Spin Frustration: A Hexanuclear Ferric Complex with a S = 5 Ground State. J. Am. Chem. Soc. 1991, 113, 6114–6124.

(18) Weighardt, K.; Pohl, K.; Jiril; Hutten, G. Hydrolysis Products of the Monomeric Amine Complex (C2H4H2N)4FeCl4; The Structure of the Octameric Iron(III) Cation of [(C2H4H2N)4Fe(μ3-O)(μ3-Cl)]12[Br4-H2O][H2O]. Angew. Chem., Int. Ed. Engl. 1984, 23, 77–78.

(19) Konar, S.; Clearefield, A. Synthesis and Characterization of High Nuclearity Iron(III) Phosphonate Molecular Clusters. Inorg. Chem. 2008, 47, 5573–5579.

(20) Kang, S.; Zheng, H.; Liu, T.; Hamachi, K.; Kanegawa, S.; Sugimoto, K.; Shioya, Y.; Hayami, S.; Mito, M.; Nakamura, T.; Nakano, M.; Baker, M. L.; Nojiri, H.; Yoshizawa, K.; Duan, C.; Sato, O. A Ferromagnetically Coupled Fe32 Cyanide-Bridged Nanocage. Nat. Commun. 2015, 6, 5955.

(21) Winpenny, R. E. P. High Nuclearity Clusters: Clusters and Aggregates with Paramagnetic Centers: Oxygen and Nitrogen Bridged Systems. In Comprehensive Coordination Chemistry II: From the biology to nantotechnology; 2nd ed.; McCleverty, J. A.; Meyer, T. J.; Ed; Elsevier: Oxford, 2004, 126–174.

(22) Berdill, I. C.; Hochdörffer, T.; Desplanches, C.; Kulmaczewski, R.; Shahid, N.; Wolny, J. A.; Warriner, S. L.; Cespedes, O.; Schümann, V.; Chatanet, G.; Halcrow, M. A. Supramolecular Iron Metallocubanes Exhibiting Site-Selective Thermal and Light-Induced Spin-Crossover. J. Am. Chem. Soc. 2019, 141, 18759–18770.

(23) Struch, N.; Bannwarth, C.; Ronson, T. K.; Lorenz, Y.; Mierent, B.; Wagner, N.; Engeser, M.; Bill, E.; Puttreddy, R.; Rissanen, K.; Beck, J.; Grimme, S.; Nitschke, J. R.; Lützen, A. An Octanuclear Metallosupramolecular Cage Designed To Exhibit Spin-Crossover Behavior. Angew. Chem., Int. Ed. 2017, 56, 4930–4935.

(24) Strohmaier, M.; Hassman, M.; Koštála, B.; Kodiček, M. MMass Data Miner: An Open Source Alternative for Mass Spectrometric Data Analysis. Rapid Commun. Mass Spectrom. 2008, 22, 905–908.

(25) Strohmaier, M.; Kavan, D.; Novák, P.; Volný, M.; Havlíček, V. MMass 3: A Cross-Platform Software Environment for Precise Analysis of Mass Spectrometric Data. Anal. Chem. 2010, 82, 4648–4651.

(26) Niedermeyer, T. H. J.; Strohmaier, M. A Software Tool for the Annotation of Cyclic Peptide Tandem Mass Spectra. PLoS One 2012, 7, e44913–e44913.

(27) SANT V6.22; Bruker AXS Inc.: Madison, WI, USA, 2000.

(28) SADABS V2.05; Bruker AXS Inc.: Madison, WI, USA, 2001.

(29) Sheldrick, G. M. SHELXT - Integrated Space-Group and Crystal-Structure Determination. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.
(30) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.
(31) Blatov, V.; Shevchenko, A. ToposPro, Program Package for Multipurpose Crystallochemical Analysis. In ToposPro V5.0, program package for multipurpose crystallochemical analysis; 2014.
(32) Van Der Sluis, P. V.; Spek, A. L. BYPASS: An Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. Acta Crystallogr., Sect. A: Found. Crystallogr. 1990, 46, 194–201.
(33) Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 9–18.
(34) Brand, R. A. Improving the Validity of Hyperfine Field Distributions from Magnetic Alloys: Part I: Unpolarized source. Nucl. Instrum. Methods Phys. Res., Sect. B 1987, 28, 398–416.
(35) Bäin, G. A.; Berry, J. F. Diamagnetic Corrections and Pascal’s Constants. J. Chem. Educ. 2008, 85, 522–536.
(36) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. PHI: A Powerful New Program for the Analysis of Anisotropic Monomeric and Exchange-Coupled Polynuclear d- and f-Block Complexes. J. Comput. Chem. 2013, 34, 1164–1175.
(37) Steckel, A.; Schlosser, G. An Organic Chemist’s Guide to Electroosmotic Mass Spectrometric Structure Elucidation. Molecules 2019, 24, 611.
(38) McInerney, J. S.; Vikse, K. L. Assigning the ESI Mass Spectra of Organometallic and Coordination Compounds. J. Mass Spectrom. 2019, 54, 466–479.
(39) Lhullier, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. SHAPE V2.1: SHAPE V2.1, Departament de Química Física, Departament de Química Inorgànica, and Institut de Química Teòrica i Computationell, Universitat de Barcelona: Barcelona, Espana, 2013.
(40) Angaridis, P.; Kampf, J. W.; Pecoraro, V. L. Multinuclear Fe(III) Complexes with Polydentate Ligands of the Family of Dicarboxy-imidazoles: Nuclearity- and Topology-Controlled Syntheses and Magneto-Structural Correlations. Inorg. Chem. 2005, 44, 3626–3635.
(41) Sunatsuki, Y.; Ohta, H.; Kojima, M.; Ikuta, Y.; Goto, Y.; Matsumoto, N.; Iijima, S.; Akashi, H.; Kaizaki, S.; Dahan, F.; Tuchagues, J.-P. Supramolecular Spin-Crossover Iron Complexes Based on Iminidazole-Iminodiacetate Hydrogen Bonds. Inorg. Chem. 2004, 43, 4154–4171.
(42) Liu, Y.; Kratsov, V.; Walsh, R. D.; Poddar, P.; Srikant, H.; Edađoudi, M. Directed Assembly of Metal–Organic Cubes from Deliberately Predesigned Molecular Building Blocks. Chem. Commun. 2004, 299, 2806–2807.
(43) Xu, Q.; Zou, R.-Q.; Zhong, R.-Q.; Kachi-Terajima, C.; Takamizawa, S. Cubic Metal–Organic Polyhedrons of Nickel(II) Iminidiazolcarboxylate Depositing Protons or Alkali Metal Ions. Cryst. Growth Des. 2008, 8, 2458–2463.
(44) Cheng, A.-L.; Liu, N.; Zhang, J.-Y.; Gao, E.-Q. Assembling the Cage-Based Metal–Organic Network from a Cubic Metalloligand. Inorg. Chem. 2007, 46, 1034–1035.
(45) Zou, R.-Q.; Sakurai, H.; Xu, Q. Preparation, Adsorption Properties, and Catalytic Activity of 3D Porous Metal–Organic Frameworks Composed of Cubic Building Blocks and Alkali-Metal Ions. Angew. Chem., Int. Ed. 2006, 45, 2542–2546.
(46) Alkordi, M. H.; Brant, J. A.; Wojtas, L.; Kratsov, V. S.; Cairns, A. J.; Edađoudi, M. Zeolite-like Metal- Organic Frameworks (ZMOFs) Based on the Directed Assembly of Finite Metal-Organic Cubes (MOCs). J. Am. Chem. Soc. 2009, 131, 17753–17755.
(47) Zhai, Q.-G.; Mao, C.; Zhao, X.; Lin, Q.; Bu, F.; Chen, X.; Bu, X.; Feng, P. Cooperative Crystallization of Heterometallic Indium-Chromium Metal-Orgnic Polyhedra and Their Fast Proton Conduction. Angew. Chem., Int. Ed. 2015, 54, 7886–7890.
(48) Yamashita, T.; Hayes, P. Analysis of XPS Spectra of Fe2+ and Fe3+ Ions in Oxide Materials. Appl. Surf. Sci. 2008, 254, 2441–2449.
(49) Monti, M.; Santos, B.; Mascareagna, A.; de la Fuente, O.; Niño, M. A.; Menteg, T. O.; Locatelli, A.; McCarty, K. F.; Marco, J. F.; de la Figuera, J. Oxidation Pathways in Bicomponent Ultrathin Iron Oxide Films. J. Phys. Chem. C 2012, 116, 11539.

(50) Carrasco, E.; Oujia, M.; Sanz, M.; Marco, J. F.; Castillejo, M. X-Ray and Ion Irradiation Effects on Azurite, Malachite and Alizarin Pictorial Models. Microchem. J. 2018, 137, 381–391.
(51) Silva, K.; Marco, J. F.; Yáñez, C. Covalent Immobilization of Amino-β-cyclodextrins on Glassy Carbon Electrode in Aqueous Media. J. Electrochem. Soc. 2019, 166, G75–G81.
(52) Haque, M. A.; Palival, L. J. Synthesis, Spectral Characterization and Thermal Aspects of Coordination Polymers of Some Transition Metal Ions with Adipoyl Bis(isonicotinoylhydrazone). J. Mol. Struct. 2017, 1134, 278–291.
(53) Peng, H.; Chen, Z.; Tong, L.; Yu, X.; Ran, C.; Liu, Z. Thermochromic Hole Burning on a Triethylammonium Bis-7,7,8,8-Tetracyanoquinodimethane Charge-Transfer Complex Using Single-Walled Carbon Nanotube Scanning Tunneling Microscopy Tips. J. Phys. Chem. B 2005, 109, 3526–3530.
(54) Shi, S.-Y.; Chen, L.-Y.; Li, Y.; He, L.-H.; Zhang, J.; Cui, X.-B. Three New Hybrid Compounds Constructed from [{PSb2Mo12O40}] Polyoxoanions, TMMC or Organic Amines. Inorg. Chem. Commun. 2019, 99, 149–155.
(55) Guseva, G. B.; Ksenofontov, A. A.; Antina, E. V.; Barannikov, V. P.; Vyugin, A. I. Crystal Solvates of Zinc(II) Bis(Dipyrrinates) with Triethylamine: Composition, Stability and Spectral-Luminescent Properties. J. Coord. Chem. 2016, 69, 901–914.
(56) Sundaresan, S.; Kühne, I. A.; Kelly, C. T.; Barker, A.; Salley, D.; Müller-bunz, H.; Powell, A. K.; Morgan, G. A. Anion Influence on Spin State in Two Novel Fe(III) Compounds: [Fe5P-Sal333])X. Crystals 2019, 9, 19.
(57) Nihei, M.; Shiga, T.; Maeda, Y.; Oshio, H. Spin Crossover Iron(III) Complexes. Coord. Chem. Rev. 2007, 251, 2606–2621.
(58) Lesconouëz, R.; Vaissermann, J.; Lloret, F.; Juve, M.; Verduga, M. Ferromagnetic Coupling between Low- and High-Spin Iron(III) Ions in the Tetranuclear Complex [Fe4(CN)2(H2O)4]2+ to [Fe4(CN)3]-: Hydrotris(1-Pryazolyl)-Borate. Inorg. Chem. 2002, 41, 5943–5945.
(59) Hoy, G. R. Relaxation Phenomena for Chemists. In Mössbauer Spectroscopy Applied to Inorganic Chemistry; Long, G. J., Ed.; Springer: Boston, MA, 1984; pp 195–226. DOI: 10.1007/978-1-4899-0462-1_8.
(60) Goura, J.-B.; Bag, P.; Mereacre, V.; Powell, A. K.; Chandrasekhar, V. Molecular Iron(III) Phosphonates: Synthesis, Structure, Magnetism, and Mössbauer Studies. Inorg. Chem. 2014, 53, 8147–8154.