Electron-deficient trifluoromethyl-substituted sub-components affect the properties of M4L4 tetrahedral cages. Struch, Niklas; Topic, Filip; Rissanen, Kari; Lützen, Arne. (2017). Dalton Transactions, 46 (33), 10809-10813. doi:10.1039/C7DT02182H
This article can be cited before page numbers have been issued, to do this please use: N. Struch, F. Topi, K. Rissanen and A. Lützen, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT02182H.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscritpts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Electron-deficient trifluoromethyl-substituted sub-components affect the properties of $M_4L_4$ tetrahedral cages

N. Struch,$^a$ F. Topić,$^b$ K. Rissanen,$^b$ and A. Lützen$^a$

Two supramolecular tetrahedral cages based on a new electron-deficient trifluoromethyl-substituted pyridylimine ligand are synthesised by sub-component self-assembly. Their structures are characterised by NMR and UV-Vis spectroscopy, high-resolution mass spectrometry and single crystal X-ray diffraction and show host-guest chemistry, complex-to-complex transformations and novel electronic properties.

Introduction

The implementation of functionality into supramolecular aggregates is one of the major challenges in modern metallo-supramolecular chemistry. This may include novel functional ligands, utilising cavities and voids in the aggregates or utilising the properties of the metal centres themselves. Complex-to-complex transformations with varying ligand systems are also a field of major interest, allowing the use of the properties of one ligand and subsequent utilization of the second ligand. Possible applications of this procedure have been shown for structurally similar but “inverted” ligand systems. Here, the electronic effects of the ligands play a major role both in supramolecular chemistry in general as well as other fields of interest, for example the field of spin-crossover research.

Hence, we focused on investigating the properties of new ligand systems in order to both adjust the binding properties of the new ligands to metal centres like iron(II) and generate new supramolecular structures.

Results and discussion

Cages 1 and 2 were synthesised in a sub-component self-assembly process (Scheme 1). A degassed mixture of 4 equivalents of pararosaniline base, 12 equivalents of 5-trifluoromethylpyridyl-2-carbaldehyde and 4 equivalents of iron(II) triflimide hydrate for 1 or zinc(II) triflimide hydrate for 2, respectively in acetonitrile was heated at 70 °C for 18 hours. A quick workup procedure of precipitating the product by addition of excess diethyl ether, filtration, washing with dichloromethane and generous amounts of diethyl ether and drying in a stream of air yielded the products in typical yields of 85%.

As shown by $^1$H- (Figure 1) and $^{13}$C-NMR spectra (SI) the structures of both cages 1 and 2 are highly symmetric, comprising a single set of signals in accordance with the structure shown in scheme 1. The UV-Vis spectra (SI) of both 1 and 2 contain the bands associated with the pararosaniline chromophore backbone (shifted by the included imine moieties and the coordinated metal centres) and the metal-N$_4$-chromophores.

Scheme 1. Synthesis of cages 1 and 2.
Furthermore, its (supra-)molecular composition was proven by high-resolution mass spectrometry (SI). Finally, the crystal structure of the mixed hexafluorophosphate (PF₆⁻) and triflate (CF₃SO₃⁻) salt of 1 was obtained. Crystals were grown from a solution of 1 with triflate as the counter-ion and an excess of KPF₆ in a mixture of acetonitrile and chloroform by gas diffusion of diisopropyl ether. The cage 1 was found to crystallise in the space group I2/a with one half of the cage in the asymmetric unit. Iron(II) metal centres exhibit the low-spin configuration, with Fe-N bond lengths between 1.966(3) and 1.986(3).

The cage was found to possess an internal cavity with a volume of 42 Å³, just big enough to accommodate a nitrate (NO₃⁻) anion. Indeed, addition of 1.2 equivalents of KNO₃ to a solution of cage 1 in acetonitrile and heating to 60°C for 1 hour resulted in the host-guest complex NO₃⁻@1 in nearly quantitative yield. Addition of one equivalent of nitrate per cage 1 and equilibrating the system for one hour yielded a mixture of empty and filled cages. □ From this experiment we could deduce a binding constant of K = 10.8 ± 1.9·10⁸ M⁻¹ (log(K)=4.03 ± 0.08). This is of the same order of magnitude as found for other, structurally similar cages. □ While the parent structure reportedly does not bind any guests the slight change in electronic properties and the added equilibration step might be the key for enabling the binding of small anions. While the slightly longer Zn-N bond length, hailing from the d⁰-configured zinc(II) centres, allows for the free rotation of aryl spacers in 2 already at room temperature, the free rotation of aryl spacers in 1 is only possible at temperatures above 313 K (SI), due to the low-spin d⁰ configuration of its Fe(II) centres.

As expected for an electron-deficient pyridylimine derivative, some properties differ from those of the parent pyridylimine structure. □ Most notably, this is a slightly different ligand field splitting at the metal centres which, while mostly irrelevant for the closed-shell dⁱ⁰-configured zinc(II) centres, has a notable impact on the properties of the iron(II) centres. Shifted ¹A₉→³T₂₈ transitions in the UV-Vis spectra (from 566 nm in the parent structure to 580 nm in 1) are observed.

Conclusions

In summary, we have synthesised and characterised two novel supramolecular tetrahedral Fe(II) and Zn(II)-based cages possessing a trifluoromethyl-substituted pyridylcarbaldehyde fragment. The tetranuclear iron(II) cage can encapsulate small anionic guests such as nitrate in its inner cavity. It furthermore exhibits novel properties such as e.g. a slight stabilization of the ³T₂₈ excited states as well as offering the possibility of complex-to-complex transformation which has not been established for aniline-backbone structures before. The presented systems were characterised by means of different NMR spectroscopic techniques, UV-Vis spectroscopy, high-resolution mass spectrometry and IR spectroscopy. Furthermore, 1 was also characterised by single crystal X-ray diffraction.

Experimental

General remarks

All substances were purchased from Alfa Aesar, J.T. Baker, Sigma-Aldrich or VWR Chemicals and used without further purification. 5-(Trifluoromethyl)-pyridyl-2-carbaldehyde was purchased from Fluorochem and used without further purification. NMR spectra were recorded on a Bruker Advance DPX 700, DPX 500 or DPX 300. Chemical shifts δ are given in...
Synthesis and characterisation of 1

A solution of 15 mg pararosaline base (0.05 mmol, 4 eq), 25 mg 5-(trifluoromethyl)-pyridyl-2-carbaldehyde (0.15 mmol, 12 eq) and 37 mg iron(III) trifluormethane (0.5 mmol, 4 eq) in 2 mL acetonitrile (HPLC grade) were degassed by one freeze-pump-thaw cycle and flushed with argon and heated to 65 °C for 18 hours. After cooling the solution to room temperature the solution was poured in 20 mL diethyl ether, the precipitate was filtered off, washed with dichloromethane and generous amounts of diethyl ether and dried in a stream of air to yield 59 mg (0.01 mmol, 85 %) purple-pink powder.

1H-NMR (acetone-d3, 298 K, 500.1 MHz, δ in ppm) = 8.84 (s, 3H, H4), 8.74 (d, JHH2=8.7 Hz, 3H, H3), 8.70 (d, JHH2=8.7 Hz, H2), 7.59 (brs, 3H, H5/6*), 7.54 (s, 3H, H1), 6.65 (brs, 3H, H5/6*), 5.81 (brs, 3H, H5/6*), 5.02 (s, 1H, H7) (*Due to the broad nature of the signals no significant cross-peaks can be observed in the 2D spectra); 13C-NMR (acetone-d3, 298 K, 156.4 MHz δ in ppm) = 176.7 (f), 160.4 (b), 153.5 (a), 149.8 (e), 147.6 (j), 140.9 (g), 138.8 (d), 131.7 (c), 130.8 (q, C3F), 123.0 (h*/i*), 121.1 (h*/i*), 120.8 (h*/i*), 118.6 (h*/i*), 80.5 (k) (*Due to the broad nature of the signals no significant cross-peaks can be observed in the 2D spectra); 19F-NMR (acetone-d3, 298 K, 282.4 MHz, δ in ppm) = -63.4 (-CF3), -79.9 (NTF); high resolution ESI-MS (acetone, positive mode, m/z) = 515.6343 (calcd. for [C6H25F2N2O]Fe(55N=O,C=Fe)5]+ 515,6341), 648.2262 (calcd. for [C6H25F2N2O]Fe(55N=O,C=Fe)6]+ 648,2260), 834.0540 (calcd. for [C6H25F2N2O]Fe(55N=O,C=Fe)5]+ 834,0546); UV-Vis (acetone, 298 K, λ in nm) = 234, 282, 326, 538, 580.

Synthesis and characterisation of 2

A solution of 15 mg pararosaline base (0.05 mmol, 4 eq), 25 mg 5-(trifluoromethyl)-pyridyl-2-carbaldehyde (0.15 mmol, 12 eq) and 37 mg zinc(II) trifluormethane (0.5 mmol, 4 eq) in 2 mL acetonitrile (HPLC grade) was degassed by one freeze-pump-thaw cycle and flushed with argon and heated to 65 °C for 18 hours. After cooling the solution to room temperature the solution was poured in 20 mL diethyl ether, the precipitate was filtered off, washed with dichloromethane and generous amounts of diethyl ether and dried in a stream of air to yield 61 mg (0.01 mmol, 86%) bright pink powder.

1H-NMR (acetone-d3, 298 K, 700.1 MHz, δ in ppm) = 8.81 (dd, JHH2=8.2 Hz, JHH2=1.6 Hz, 3H, H3), 8.54 (s, 3H, H4), 8.46 (d, JHH2=8.2 Hz, 3H, H2), 8.34 (brs, 3H, H1), 7.16 (d, JHH2=8.4 Hz, 6H, H5), 5.99 (d, JHH2=8.4 Hz, 6H, H6), 4.71 (s, 3H, H7); 13C-NMR (acetone-d3, 298 K, 156.4 MHz δ in ppm) = 165.7 (f), 148.9 (b), 147.3 (a), 146.7 (g), 146.6 (j), 141.3 (i), 131.7 (q, -CF3), 131.3 (c), 128.7 (i), 123.0 (h), 120.6 (e), 80.7 (k); 19F-NMR (acetone-d3, 298 K, 282.4 MHz δ in ppm) = -63.5 (-CF3), -80.13 (NTF); high resolution ESI-MS (acetone, positive mode, m/z) = 420.936 (calcd. for C16H12O3F2N2O2Zn4 420,936), 521.059 (calcd. for [C6H25F2N2O]Zn(55N=O,C=Fe)3]+ 521,058), 654.554 (calcd. for [C6H25F2N2O]Zn(55N=O,C=Fe)2]+ 645,576), 841.649 (calcd. for [C6H25F2N2O]Zn(55N=O,C=Fe)3]+ 841,649), 1122.041 (calcd. for [C6H25F2N2O]Zn(55N=O,C=Fe)4]+ 1122,040); UV-Vis (acetone, 298 K, λ in nm) = 230, 286, 342, 504, 530.

Transformation from 1 to the parent structure

A solution of 10.0 mg (0.0017 mmol, 1 eq) 1 and 2.5 mg (0.023 mmol, 13.2 eq) pyridyl-2-carbaldehyde in 0.6 mL acetone-d3 was heated to 50 °C for 18 hours. The resulting mixture was analysed by NMR-spectroscopy. Afterwards the solution was poured in diethyl ether, filtered, the remaining precipitate was washed with dichloromethane and diethyl ether and dried in a stream of air to yield the pure parent compound in 6 mg (0.0013 mmol, 72%) isolated yield. The resulting 1H-NMR spectrum is in accordance with previously published NMR data.

Synthesis and characterisation of NO3@1

A solution of 10.0 mg (0.0017 mmol, 1 eq) 1 and 0.17 mg (0.0011 mmol, 1.0 eq) KNO3 in 0.6 mL acetone-d3 was heated to 60 °C for 2 hours and the resulting solution was analysed by NMR spectroscopy.

1H-NMR (acetone-d3, 298 K, δ in ppm) = 8.65 – 8.75 (m, 6 H, H2/H3), 8.70 (s, 3 H, H4), 7.53 (s, 3 H, H1), 7.50 (brs, 6 H, H5/6*), 5.47 (brs, 6 H, H5/6*), 4.76 (s, 1H, H7) (*Due to the broad nature of the peaks no significant cross peaks could be assigned in the 2D spectra); 13C-NMR (acetone-d3, 298 K, 156.4 MHz δ in ppm) = 175.5 (f), 160.8 (b), 153.1 (a), 149.2 (e), 147.1 (j), 140.8 (g), 138.4 (d), 130.7 (c), 130.6 (q, C3F), 122.0 (h*/i*), 120.7 (h*/i*), 120.3 (h*/i*), 118.9 (h*/i*), 81.1 (k) (*Due to the broad nature of the peaks no significant cross peaks could be assigned in the 2D spectra); 19F-NMR (acetone-d3, 298 K, 282.4 MHz, δ in ppm) = -65.4 (-CF3), -79.9 (NTF); high resolution ESI-MS (acetone, positive mode, m/z) = 484.503 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)5]+ 484,501), 575.752 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)6]+ 575,582), 703.101 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)2]+ 703,101), 746.687 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)(55N=O,C=Fe)5]+ 746,685), 790.471 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)(55N=O,C=Fe)4]+ 790,469), 1003.586 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)(55N=O,C=Fe)4]+ 1003,581), 1504.065 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)(55N=O,C=Fe)4]+ 1504,060), 1058.068 (calcd. for [NO3@C6H25F2N2O]Fe(55N=O,C=Fe)(55N=O,C=Fe)4]+ 1058,065); UV-Vis (acetone, 298 K, λ in nm) = 235, 275, 337, 543, 583. Due to the procedure without any purification a small amount of free ligand can be observed.
Crystallographic analysis of 1_Pn6Tfo

Single crystal X-ray diffraction data were collected on an Agilent SuperNova Dual diffractometer with an Atlas detector using mirror-monochromatized Cu-Kα radiation (λ = 1.54184 Å) from a microfocus source, equipped with an Oxford Cryostream cooling system. CrysAlisPro\textsuperscript{13} software was used for data collection, integration and reduction as well as applying the analytical and semi-empirical absorption corrections.

The structures were solved by direct methods using SHELXT\textsuperscript{14,15} and refined by full-matrix least-squares using SHELXL-2016/6\textsuperscript{16} within the OLEX2\textsuperscript{17} and WinGX\textsuperscript{18} environment. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined as riding on the parent carbon atoms with U_H = 1.5 U_C (for methyl groups) or U_H = 1.2 U_C otherwise. PLATON\textsuperscript{19} was used for the accurate calculation of geometrical parameters, while the figures were generated using Mercury\textsuperscript{20} and QuteMol.\textsuperscript{21}

All the ligands’ trifluoromethyl (–CF\textsubscript{3}) groups’ geometries were restrained, with all C–F bonds as well as F–F and C–F distances restrained to be equal. Two of the –CF\textsubscript{3} groups were also modelled as disordered over two components each, with respective occupancies refining to 0.540(19)/0.460(19) and 0.565(9)/0.435(9). Out of expected anions, only three anion-occupied positions were modelled, one of which with half-occupancy. Their geometries were restrained to be regular and identical, while the CF\textsubscript{3}SO\textsubscript{3} anion was modelled as a rigid body using the coordinates extracted from a published structure, CSD refcode MEFHOW.\textsuperscript{21} Their atomic displacement parameters were also appropriately restrained.

Moreover, three acetonitrile molecules could be located and modelled, one of which with half-occupancy. Their geometries were restrained to be the same, and the rigid-body restraints were applied to their atomic displacement parameters. Finally, the rest of the solvent molecules were found to be too badly disordered and could not be modelled explicitly. The SQUEEZE\textsuperscript{22} routine of PLATON\textsuperscript{8,23} was used to calculate the contribution of electron density in these regions to the structure factors in form of FAB files which were used in subsequent refinement cycles.

Crystal dimensions 0.415×0.244×0.190 mm\textsuperscript{3}, dark violet block, C\textsubscript{170}.72H\textsubscript{121}.20Fe\textsubscript{23}Fe\textsubscript{2}N\textsubscript{22}O\textsubscript{17}.P\textsubscript{3}S\textsubscript{6}.0.75. M = 4172.09, monoclinic, space group I2/a, a = 39.5026(9), b = 21.4950(6), c = 30.4701(9) Å, α = 90°, β = 90.077(2), γ = 90°, V = 25872.41(12) Å\textsuperscript{3}, Z = 4, ρ = 1.071 g cm\textsuperscript{-3}, μ = 2.816 mm\textsuperscript{-1}. F(000) = 8402, 43952 reflections (2θ\textsubscript{max} = 148.67°) measured (24229 unique, R\textsubscript{int} = 0.0266, 96.2% completeness at 2θ\textsubscript{max} = 135.5°), Final R indices (I > 2σ(I)): R\textsubscript{i} = 0.1138, wR\textsubscript{i} = 0.3161. GOF = 1.283 for 1479 parameters and 2203 restraints, largest diff. peak and hole 2.543/−1.494 eÅ\textsuperscript{-3}. CCDC-1540569 contains the supplementary data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/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.

Acknowledgements

Financial support from DFG (SFB 813 – Chemistry at Spin Centers) and the Academy of Finland (K.R.: project no’s. 263256, 292746 and 265328) is gratefully acknowledged. N.S. thanks Evonik Foundation for a doctoral scholarship.

Notes and references

\dagger Please note: Here, “inverted” means that the structure-forming backbone consists of linked pyridylcarbaldehyde structures and the ligand is formed by the addition of aniline derivatives. See Ref. 11.


9. The tetranuclear zinc(II) cage 2 decomposes upon exposure to nitrate ions.


Two supramolecular cages based on a trifluoromethyl-substituted pyridylimine ligand have been synthesised that show host-guest chemistry and complex-to-complex transformations.